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Syntheses of Some Cyclopropenes and a Study of the ir Mode of Rearrangement Using Homogeneous Catalysts

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THE STUDY OF THE HOMOGENEOUS ISOMERIZATION OF SUBSTITUTED PHENYLCYCLOPROPANES WITH DI-μ-CHLOROTETRACARBONYLDIRHODIUM(I)

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ABSTRACT

The rates of homogeneous isomerization of a series of phenylcyclopropanes in the presence of catalytic amounts of $[Rh(CO)_2Cl]_2$ were observed to be dependent on the structure of the phenylcyclopropanes. The mechanism of the isomerization is discussed. The rate of the isomerization and the nature of the products from the isomerization are interpreted in terms of conjugative and steric factors for the substrate and the stability of the intermediates of the isomerization.

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INTRODUCTION

In the study of the field of small ring compounds, cyclopropanes are found to undergo ring-opening reactions over transition metal and transition metal ion catalysts. Palladium metal is one of the catalysts reported in 1970/1/. Later, it was found that conjugative and steric effects on the ring-opening reaction of substituted phenyl-cyclopropane over palladium metal significantly affect the products of the reaction. Conjugative effects were concluded to outweigh steric effect in the ring-opening reaction/2/. Homogeneous isomerization of vinylcyclopropanes in the presence of di-μ-chlorotetracarbonyldirhodium ($[Rh(CO)_2Cl]_2$) was reported in 1974/3/ and the general principles of the catalysis were discussed /4/. The action of the catalyst in promotion of the reaction was discussed in terms of the molecular orbital (M.O.) theory/4/, especially orbital symmetry considerations. The correlation of the M.O. of the reaction product(s) and the reactant(s), in terms of M.O. symmetry, was deduced from the theory of Woodward and Hoffmann/5/.

The molecular transformation consists of the breaking of certain bonds between atoms and the formation of new bonds. A flow of electrons from the highest occupied M.O. (HOMO) of the reactant(s) to the lowest unoccupied M.O. (LUMO) of the product(s) takes place as the reaction occurs.

The electrons follow the transition path with the lesser energy of activation. The electron movement between the HOMO of the reactant and the LUMO of the product was found to obey orbital symmetry rules. The new M.O. which the electrons occupy must have the same symmetry as the M.O. the electron was in before the movement. A correlation diagram for the symmetry-allowed (thermally permitted) reaction is given in Figure 1.

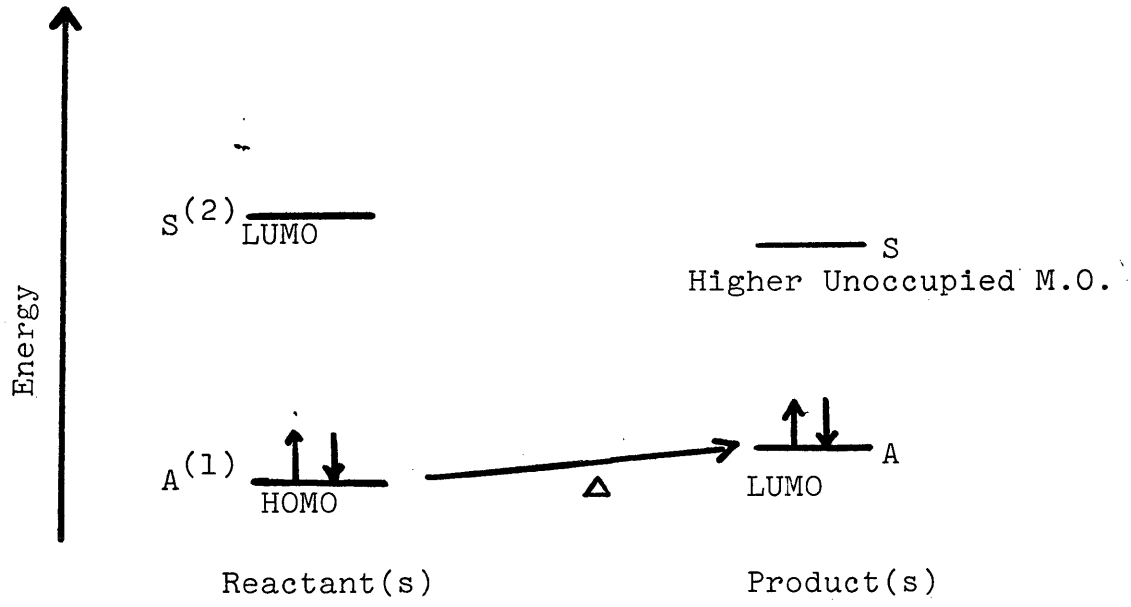


Figure 1. Correlation of a Symmetry-Allowed Reaction

If the symmetry properties of the HOMO of the reactant are different from that of the LUMO of the product, the electron in the HOMO of the reactant will enter the M.O.

(1) A: Antisymmetric
(2) S: Symmetric

of the product but, in higher energy level than the LUMO of the product which has different symmetry properties. In such case, more energy has to be provided to the system in order to promote the reaction, that is, a photo-permitted process. The correlation diagram of the M.O. of the symmetry "forbidden" (photo-permitted) process is illustrated in Figure 2.

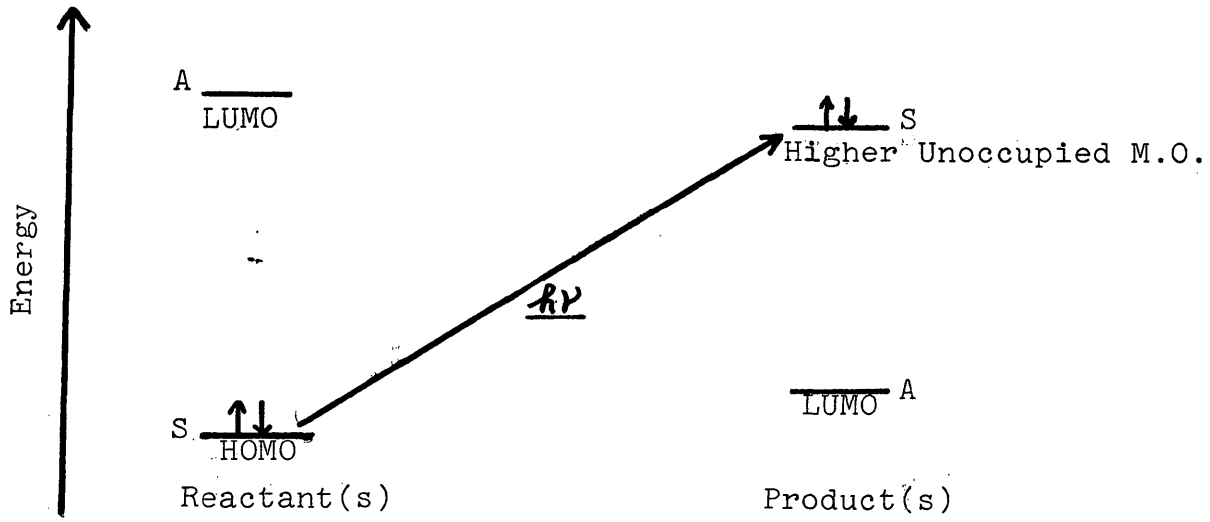


Figure 2. Correlation Diagram of a Symmetry-Forbidden (Photo-permitted) Reaction.

However, metals (or their ions) can provide an available M.O. with the same symmetry as the LUMO of the product(s), and the energy of activation of the reaction is decreased by the action of the catalyst as illustrated in Figure 3.

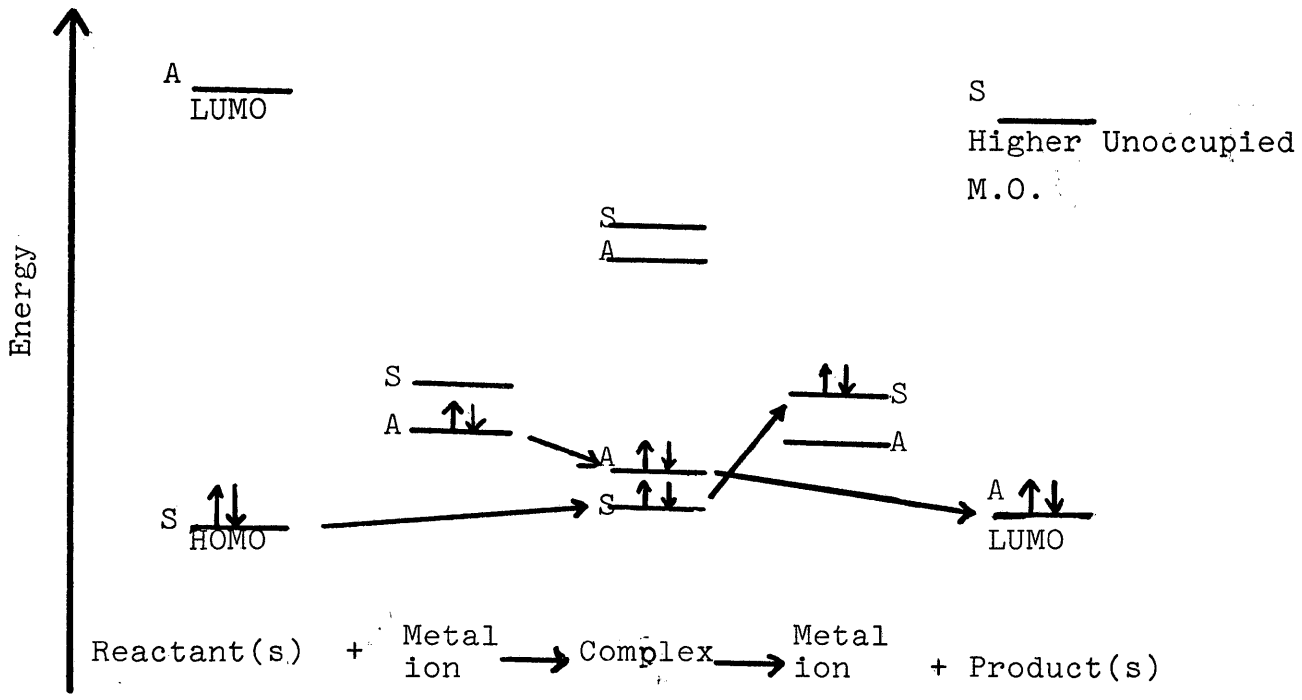


Figure 3. The Correlation Diagram of M.O. in a Metal Catalytic Reaction /4/

The π M.O.'s of cyclopropane in the ground state have been proposed to have the configurations listed in Figure 4/6/. Also the M.O. of the conjugated vinylcyclopropane, proposed by Pasto, Chen and Binsch/6/, is listed in Figure 4. A highly strained cyclopropane ring model was proposed for the M.O. of the cyclopropanes.

Several examples of metal catalyzed valence isomerization have been reported/3,7,8/.The work of Voigt and Roth/3/, concerning the isomerization of vinylcyclopropanes, is of special interest here. Examples are given in the following reactions:

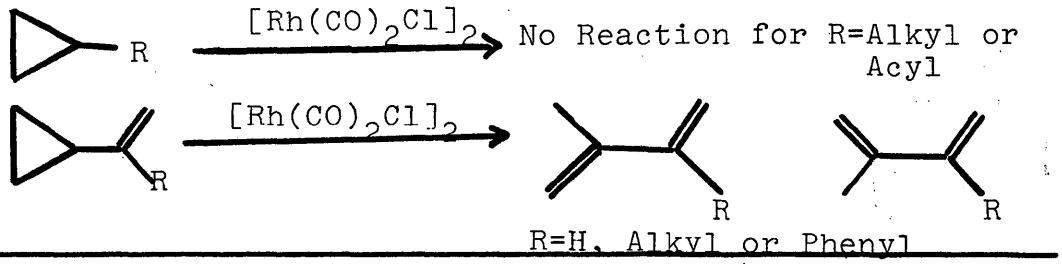
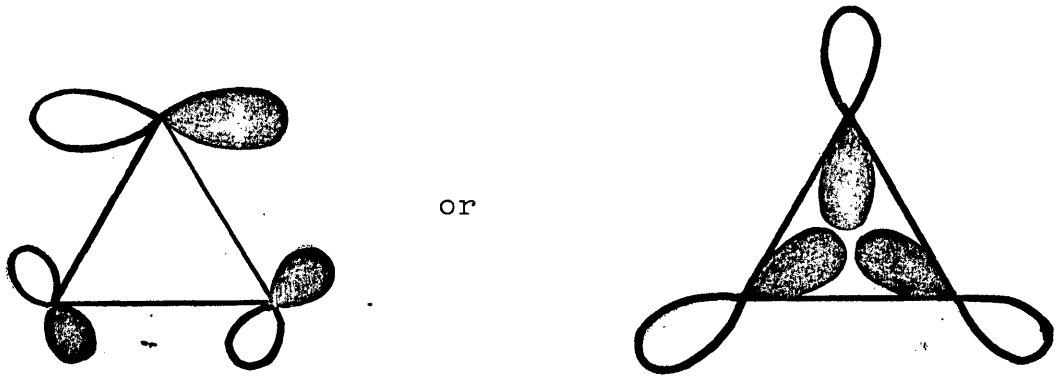
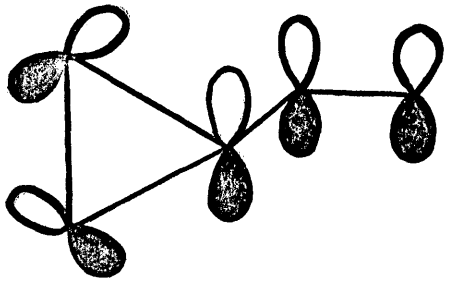


Figure 4. The M. O. Diagram of Cyclopropane and Conjugated Vinylcyclopropane



or

Cyclopropane



Conjugated Cyclopropane

Explanation:  The black lobe represents the positive sign of the wave function, the white lobe represents the negative sign of the wave function.

In Voigt and Roth's work, the conclusion is given that attachment of vinyl to the cyclopropyl group (to provide the maximum conjugation of p-orbitals of vinyl and cyclopropyl) is the primary requirement for the occurrence of the isomerization reaction. A metal catalyst is necessary for the isomerization reaction in order to use the metal d-orbitals to alter the symmetry "forbidden" pathway.

In the homogeneous isomerization of vinylcyclopropane, a carbonium ion was proposed to be the intermediate of the reaction/3/. The study of geometries and energies of $C_3H_7^+$ cations by Radom and Pople/9/ shows the "allyl type" $C_3H_7^+$ cation may have the highest energy state. The relative energy diagram of the various $C_3H_7^+$ cations is shown in Figure 5.

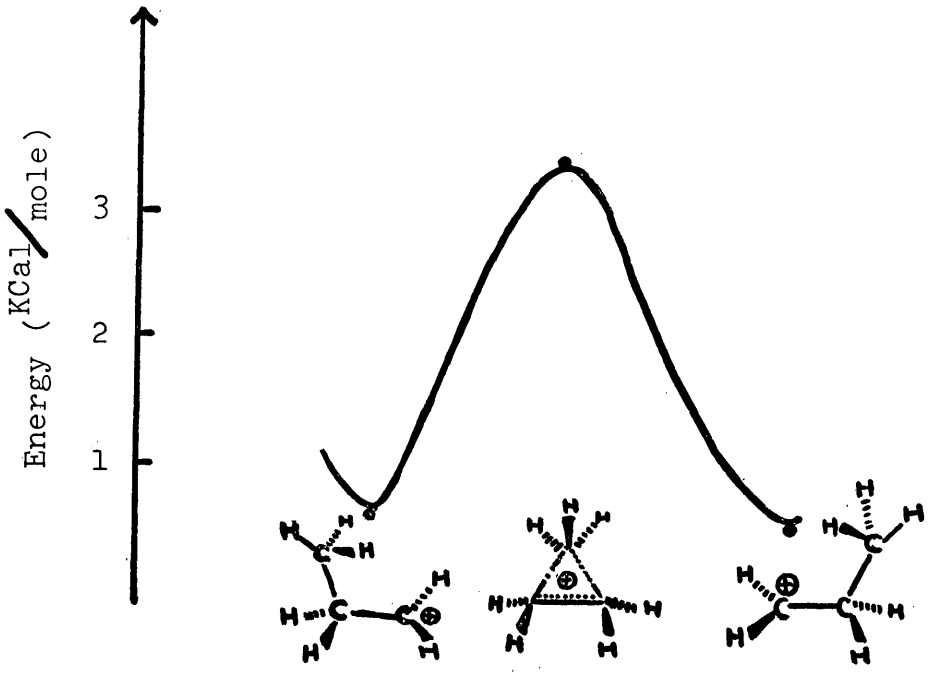
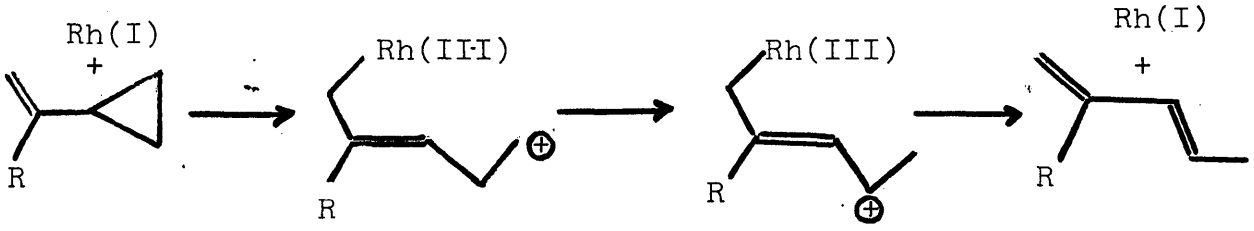


Figure 5. Relative Energy Diagram of $C_3H_7^+$ Cation/9/

According to the above study, the intermediate carbonium ion in the isomerization reaction of vinylcyclopropanes may be a classical carbonium ion because, in terms of stability, the classical carbonium ion may be more stable than the "allyl type" carbonium ion of the cyclopropyl.

The mechanism of the ring-opening of vinylcyclopropanes was proposed to be a step-wise mechanism, as in the following illustration:



A 1,2 hydride shift was suggested to be one of the steps in the isomerization reaction.

A study of partial rate factors for the nitration of phenylcyclopropane derivatives by Stock and Young/10/ showed that the conformation of the phenylcyclopropane molecule affects the activity towards electrophilic substitution reaction. The results were found to be due to the degree of conjugation between the phenyl and the cyclopropyl groups of the phenylcyclopropanes, determined by the steric effect. The relative activities of phenylcyclopropane in nitration reaction with respect to the conformation of the molecule

are listed in Table 1.

Table 1. Relative Activities of Phenylcyclopropane towards Electrophillic Substitution

Conformation of Phenylcyclopropane		 Perpen-dicular	 Angular	 Bisected
Relative Activities	1.0	13-30	950	1800
Relative Ability of Conjugation between Phenyl and Cyclopropyl		Not Possible	Very low	Maximum Conjuga-tion

Of this study, the result that conjugation of phenyl and cyclopropyl in phenylcyclopropane caused the increase of the rate of electrophillic substitution is not surprising.

According to Roth and Voigt's results/4/, phenylcyclo-propanes may be also affected by a conjugative effect in the homogeneous isomerization. The activity of phenycyclopro-panes in the homogeneous reaction decreases whenever the condition for the "bisecting" conformation is not satisfied.

Steric hinderance is one of the effects that will affect the conformation. In such cases, the rate of homogeneous isomerization may be affected by the steric hinderance.

In this thesis, the conjugative and the steric effect of the isomerization of phenylcyclopropanes is studied. According to the kinetic study and the study of the nature of the products from the isomerization of phenylcyclopropanes, it is possible to propose a mechanism of this reaction.

EXPERIMENTAL

INSTRUMENTAL

Nuclear magnetic resonance (NMR) spectra were recorded with a Varian A-60 high resolution NMR spectrometer. The samples were analyzed as the neat liquid or in solution with chloroform-d(Diaprep Inc., Atlanta, Ga., minimum isotopic purity: 99.8%) or carbon tetrachloride (spectroquality, Matheson, Coleman and Bell, East Rutherford, N.J.). Chemical shifts are recorded as ppm(δ) from tetramethylsilane (TMS,δ=0.00) as an external standard.

Both analytical and preparative gas phase chromatography (G.C.) were performed with a Varian Aerograph Model A90-P, equipped with a thermal conductivity detector, connected to a Sargent-Welch recorder (model SRG). The sensitives for the instruments were at least 0.1% at a full range scale of 1.0 millivolt. The on-column injection technique was used. Helium was used as carrier gas with a constant external pressure of 20 p.s.i. to produce a flow rate of 40-60 milliliters per minute. Analytical gas chromatography peak areas were determined by triangulation. Retention times of the components were reported in minutes with respect to the time of sample injection. All columns used were newly constructed, using

¼ inch (OD) copper tubing. Column composition was expressed as a weight/weight percent of stationary phase to the supporting material.

Infrared (IR) spectra were obtained with a Perkin-Elmer Model 337 Spectrophotometer using potassium bromide plates. The spectra were recorded as liquid films of neat liquids.

The isomerization reactions were allowed to proceed in a well stirred constant temperature oil bath equipped with a thermostat, Precision Porta Temp (Scientific Company N.Y.). The temperature of the oil bath was maintained at 90±1°C measured by a mercury thermometer.

The IR spectral data represent the diagnostic absorptions only. The NMR spectra were interpreted as first order. Results from gas chromatographic analysis are described at a given condition: column length, retention time of the component and relative area represented by the component of the chromatogram.

PREPARATIONS

Methylene Iodide (Methane, diiodo-) (I) was prepared from 100 gram of iodoform (Aldrich, 98%), 27.4 g . of C.P. arsenious oxide (J.T. Baker, N.J.), 40 g of sodium hydroxide and 120 cc of water as solvent, following the method described by Adams & Marvel /11/. Eighty gm. of pure methylene iodide was obtained under reduced pressure distillation at 106°C/70τ.

Deutero-Methylene Iodide (CD_2I_2) (II) was prepared by the same procedure as above from the reaction of 100 gm. of iodoform (Aldrich, 98%), 27.4 g . of C.P. arsenious oxide (J.T. Baker, N.J.), 40 gm of 99+ atom %D sodium deuteroxide, (Diaprep Inc., Milwaukee Wis.) and 120 cc of D_2O (Diaprep Inc., Wis.) as solvent. The product was purified by reduced pressure distillation. Yield was 80%. The isotopic purity was determined by NMR by comparing the singlet integration to a pure dihydro methylene iodide sample. The NMR spectrum (25% solution in $CDCl_3$) showed absorption at δ=3.9 for both methylene iodide and deutero-methylene iodide. The isotopic purity was determined to be about 85% pure.

Vinylcyclopropane (III) The procedure was adopted from the LeGoff modification of the Simmons-Smith Reaction/12/.

Zinc-copper couple was prepared by the method described by LeGoff/13/ from 35 g. of zinc dust (J. T. Baker N.J.) and 2.0 gm. of cupric acetate monohydrate (J. T. Baker, N.J.)

To 30 ml. of p-dioxane (Spectrophotometric Grade, Aldrich, Milwaukee) in a pressure bottle, 3.6 g. (0.07 mole) of butadiene (Phillips 66, 99.5% mole purity), 15 g. (0.06 mole) of methylene iodide (I) and 3.2 g. of Zn-Cu couple were added at dry-ice temperature. Then a small crystal of sublimated iodine was added and the pressure bottle was sealed to a Parr pressure reaction apparatus (Parr Apparatus, Illinois) provided with heating and shaking devices. The mixture was heated to 60°C and was shaken for 48 hours. The bottle was opened and the contents were decanted through glass wool.

The bulk of p-dioxane was removed by distillation in a constant temperature (45°C) bath and the receiver was kept at dry-ice bath temperature.

Isolation of vinylcyclopropane (III), butadiene, methylene iodide and p-dioxane was by gas chromatography on a 6 ft. x ¼ in. column of 10% SE-30 on 60/80 chromosorb-P,

maintained at 65°C and using a helium flow at 20 p.s.i. of external pressure.

The retention times were: butadiene 1.7 min., vinylcyclopropane 3.2 min., dicyclopropyl 7.5 min., methylene iodide and p-dioxane 15 min. (with a very long tail). Percentage yield of vinylcyclopropane was 33% and of dicyclopropyl was 5%.

The NMR spectrum (40% solution in CCl_4) gave complex multiplets at δ=0.1 to 0.9 (4H), δ=1.2 to 1.7 (1H), and δ=4.8 to 5.7 (3H).

1-Methyl-1-isopropenylcyclopropane (IV) Fifty ml. of anhydrous ether (Fisher Scientific Co., N.J.), together with 15 g. of Zn-Cu couple was put into a 100 ml. two necked round-bottom flask, fitted with a refluxing condenser which connected to a calcium chloride drying tube. A small iodine crystal was put into the flask and a dropping funnel was fitted into the flask at the same time. Two milliliters of methylene iodide was added from the dropping funnel and the mixture in the round-bottom flask was heated at the refluxing temperature for about 5 minutes. The rest of the methylene iodide, 7.67 ml (a total amount of 9.67 ml. or 0.12 mole) was mixed with 8.21 g. (0.1 mole) of 2,3-dimethylbutadiene-1,3 (practical grade, J. T. Baker, N. J.). The mixture was added into the round-bottom flask through the dropping funnel for a period of one to 1¼ hours.

After 10 hours of refluxing, about 1.0 ml of methylene iodide and 0.5 g. of Zn-Cu couple was added into the mixture. The mixture was refluxed for 20 hours more. G.C. analysis of the mixture demonstrated that there was 15% yield of product.

The mixture was distilled by reduced pressure (polymerization occurred). The distillate was again analyzed by G. C. with a 10% SE-30 on 60/80 Chromosorb-P (6 ft. x ¼ in.) column at a temperature of 80°C and helium at 20 p.s.i. external pressure. The retention times of the component of the mixture were: ether 2.5 minutes, 2,3-dimethylbutadiene-1,3 4.25 min., 1-methyl-1-isopropenyl-cyclopropane 5.5 min. The product was isolated and purified under the same G. C. conditions. The NMR spectrum (5% solution in CCl_4) gave a broad singlet at δ=4.4 (2H), singlets at δ=1.4 (3H) and δ=1.0 (3H), and multiplets at δ=0.0 to 3.0 (4H).

Cis-1-phenyl-2-methylcyclopropane (V) was prepared by the same procedure as above from the reaction of 5.90 g. (0.05 mole) cis-propenylbenzene (99% pure, Chemical Samples Co., Ohio), 6.5 ml. (0.07 mole) methylene iodide and 4.0 g. Zn-Cu couple, using 25 ml. of anhydrous ether (Fisher Scientific Co., N. J.) as solvent.

The mixture was allowed to reflux for 3 hours, then one-half ml. of methylene iodide and ¼ g. of fresh Zn-Cu couple was added into the mixture.

The mixture was allowed to reflux for 33 hours more. G. C. analysis to monitor product formation was done from time to time and a maximum yield of 85% of product was obtained after a total refluxing time of 36 hours.

Both analytical and preparative G.C. were done by using a 6 ft. x ¼ in. column of 10% SE-30 on 60/80 Chromosorb-P. Column temperature was maintained at 135°C. Retention times of the components in the mixture were observed to be: ether 0.9 min., methylene iodide 3.5 min., cis-propenylbenzene 5.5 minutes, cis-1-phenyl-2-methyl-cyclopropane 9 min.

The NMR spectrum (25% solution in $CDCl_3$) gave a sharp singlet at δ=7.2 (5H), a complicated multiplet at δ=1.8 to 2.1 (1H) and multiplets a δ=0.4 to 1.0 (6H).

Trans-1-phenyl-2-methylcyclopropane (VI) Similarly, from the reaction of 5.90 gm. (0.05 mole) of trans-β-methylstyrene (Aldrich, Milwaukee, Wis.), 6.5 ml (0.07 mole) methylene iodide and 4.0 gm. of Zn-Cu couple, refluxing in 25.0 ml of anhydrous ether (Fisher Scientific Co., N.J.),

trans-1-phenyl-2-methylcyclopropane (VI) was obtained. Total yield calculated from the G. C. analysis was 75% after refluxing for 35 hours.

Both preparative and analytical gas chromatography was done by using a 6 ft. x ¼ in. column of 10% SE-30 on 60/80 Chromosorb-P. Column temperature was maintained at 140°C. Retention times of the components in the mixture were: ether 1.0 min., methylene iodide 4.7 min., trans-β-methylstyrene 8.2 min., trans-1-phenyl-2-methylcyclopropane 10.9 min. Percentage purity of the product isolated by the G. C. was found to be more than 98%.

The NMR spectrum (50% solution in CCl_4) gave a doublet at δ=7.0 (5H), multiplet a δ=1.1 to 1.5 (1H), and multiplet at δ=0.2 to 1.0 (6H).

1-phenyl-1-methylcyclopropane (VII) Similarly, from the reaction of 14.16 g. (0.15 mole) of iso-propenylbenzene (tech. grade, Chemical Sample Co., Ohio), 37.5 g. (0.14 mole) of methylene iodide and 15 gm. of Zn-Cu couple, using 50 ml. of anhydrous ether (Fisher Scientific Company N.J.) as solvent, 1-phenyl-1-methylcyclopropane was obtained.

The mixture was refluxed in a 250 ml. three necked round-bottom flask under dry nitrogen atmosphere to prevent

polymerization[1]. The yield was 91.5% after refluxing for 36 hours.

G.C. analysis of the product on a 6 ft. x ¼ in. column of 10% SE-30 on 60/80 Chromosorb-P at a column temperature of 135°C. The retention times of the components of the mixture were: ether 1.5 min., methylene iodide 5.5 min., iso-propenylbenzene 7.2 min., 1-phenyl-1-methylcyclopropane (VII) 8.8 min. Preparative G.C. afforded the 98% pure product after reinjection and collection.

The NMR spectrum (neat liquid) gave a singlet at δ=6.8 (5H), singlet at δ=1.0 (3H), and multiplets at δ=0.1 to 0.6 (4H).

The IR Spectrum (neat liquid, cell path 0.05 mm) gave absorption peaks at 3211 cm^{-1} (aromatic ring), 3000 cm^{-1} (alkane and alkene), 2000 cm^{-1} to 1660 cm^{-1} (mono-substituted aromatic 'finger prints') and 1020 cm^{-1} (cyclopropyl C-H).

(1) The dry nitrogen atmosphere seemed to be very critical in the above synthesis work. The synthetic work had been done several times by the author and if not under nitrogen atmosphere, it was found that the reaction mixture tended to polymerize in the open air and almost no product was isolated.

Preparation of the Catalytic Solution (1.286×10^{-3} molar solution of $[Rh(CO)_2Cl]_2$). Spectrograde quality chloroform-d (Diaprep Inc., Atlanta, Ga., minimum isotopic purity: 99.8%) was used as solvent after degassing under reduced pressure, ca 10.0 torr. Rhodium dicarbonyl chloride dimer was obtain from Strem Chemicals Inc., Danvers, Mass. The dimer (1.0 gm in a sealed vial) was shipped under an argon atmosphere. Manipulations of the dimer were conducted in a dry box (Hamilton Manufacturing Co., Wis.) under a nitrogen atmosphere as suggested by Shriver /14/.

The catalytic solution was prepared by dissolving 10.0 mg of the dimer in 20.0 ml of the above chloroform-d, following the procedure described by H.W. Voigt /4/. The $[Rh(CO)_2Cl]_2$ solution was stored in a dry box under a nitrogen atmosphere for the whole period of the experiment.

Substrates. Phenylcyclopropane (VIII) (98.5%, Aldrich, Wis.), 1-phenyl-1-methylcyclopropane (VII), cis-1-phenyl-2-methylcyclopropane (V), trans-1-phenyl-2-methylcyclopropane (VI), and trans-1,2-diphenylcyclopropane(1) (IX) were purified to greater than 98% by preparative gas chromatography.

(1) A sample of Compound (IX) was obtained from Dr. J. A. Roth.

ISOMERIZATION METHOD

Apparatus and Procedures. The stock solution of catalyst, the substrates, and some NMR tubes were put in the dry box. In the metal part of the dry box, a Dewar flask, with dry-ice in isopropyl alcohol was made ready for use.

One-half milliliter of the substrate was transferred to the NMR tube, flushed by a stream of nitrogen gas for ½ min., then followed by 1.0 ml. of the catalytic solution. The NMR tube was again flushed by a stream of nitrogen for one minute, the cap was put on, and the tube was transferred to the dry-ice bath in the metal part of the dry box. Nitrogen pressure was then adjusted to above 2 to 3 atm. pressure for 5 minutes in the metal part of the dry box in order to let more nitrogen gas "leak in" from the cap of the NMR tube, in case there was any leakage of the cap to the tube.

The NMR tube was then removed from the dry box to the opened air and the tube was sealed by a torch immediately with the cap on. A NMR spectrum was run as the reference point for a kinetic run (reaction time equal to zero). The tube was then put in the reaction oil bath.

Monitoring the Formation of the Products. NMR spectra of the reaction mixtures were taken from time to time in order

to monitor the percentage of isomers and for calculation of the reaction rate by the integration of the peak areas.

On completion of the reaction, the sample tube was opened. The mixture was injected through the G.C. Peak areas were calculated to determine the percentage of the isomers again. Individual product peaks were collected after multiple injection into the G.C. NMR spectra were obtained for individual isomers for the purpose of identification.

Rate of Reaction. Reaction rate was expressed as the number of millimoles reacted per unit time. Calculation was based on the integration of the NMR spectra in which the decrease in the protons of the substrate or the increase of protons of the products was detected and the integrations compared. G.C. analysis was used for calculation of the percentage of the final product after the completion of the reaction. Examples of calculation of the rate of reaction by NMR integration is listed in Table 2.

Table 2. Example of Calculation of Rate of Isomerization Reaction of Phenylcyclopropane (VIII)[1]

TIME (days)	Chemical Shifts from TMS (δ=0.0)	Integration (Units)	Percent of(VIII) Reacted	# of m-mole Reacted	Reaction Rate (mmole/day)
0.00	7.1	75(5H)	0.0	0	
	0.3-0.8	60(4H)			
20.0	7.1	95(5H)	34.2%	1.37	6.84×10^{-2}
	0.3-0.8	50(2.63H)			

(1) Number of mmole initially was 4.0 mmole

RESULTS

Kinetic data: The kinetic data for the isomerization reaction of phenylcyclopropane(VIII), trans-1-phenyl-2-methylcyclopropane (VI), cis-1-phenyl-2-methylcyclopropane(V), 1-phenyl-1-methylcyclopropane(VII) and trans-1,2-diphenylcyclopropane (IX) are listed in Table 3.

The NMR spectra for a defined point of a kinetic run of the compounds are listed in Appendix 1A to Appendix 12B.

Table 3. Kinetic Data for the Isomerization Reaction of Compound (VIII), (VI), (V), (VII), and (IX)

Substrate	Average Rate (mmole/day)	Relative Rate	Reaction Temperature	$\frac{[\text{Substrate}]}{[\text{Catalyst}]}$ (1)
(VIII)	7.01×10^{-2}	1.00	90±1°C	3.11×10^{3}
(VI)	9.50×10^{-1}	13.5	90±1°C	2.95×10^{3}
(V)	2.70×10^{-2}	0.38	90±1°C	2.95×10^{3}
(VII)	0.00×10^{-2}	0.00	90±1°C	2.95×10^{3}
(IX)	1.43×10^{-1}	2.03	90±1°C	2.95×10^{3}

(1) Number of mmole of compound (VIII) initially was 4.0; of compounds (V), (VI) and (VII) was 3.8 mmole; of compound (IX) was 3.0 mmole.

Products from the Isomerization of Phenylcyclopropane(VIII)

Phenylcyclopropane(VIII) was quantitatively isomerized to three components. NMR analysis of the products indicated trans-β-methylstyrene(VIIIA) was the major product. Cis-propenylbenzene(VIIIB) and α-methylstyrene(VIIIC) were the minor products. From the integration of the peak areas, the NMR spectra indicated 20% of α-methylstyrene was obtained from the isomerization reaction. G.C. analysis(1) of the product mixture gave two components (A and B) with equal area. These two components were isolated and purified by preparative G.C. at the same conditions as the analytical G.C. NMR and G.C. analysis of the two components are summerized in Table 4A, Table 4B and Table 4C.

(1) G.C. conditions: 6 ft. x ¼ in. 10% SE-30 on 60/80 chromosorb-P, column temperature 135°C.

Table 4A G.C. Analysis of the Product Components From the Isomerization of (VIII)

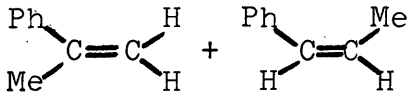
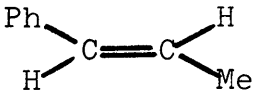
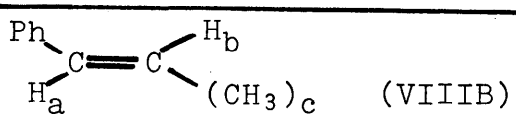
	G.C. Component A	G.C. Component B
Product		
Retention time	6.2 min	7.3 min
Percentage(1)	50.0% (20.0%*+30.0%)	50.0%

Table 4B NMR Analysis(2) of G.C. Component B, Chemical Shifts from TMS (δ=0.0)

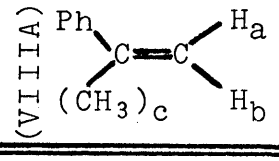
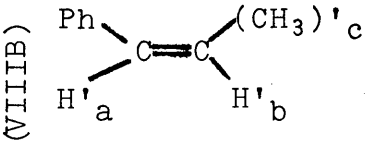
Product	 (VIIIB)
Chemical Shift (δ)	Identification of PROTON
7.2 (m) (5H)	Phenyl group
6.3-6.0 (m) (2H)	H_a and H_b
2.0 (d) (3H)	$-(CH_3)_c$ (J^3=5 Hz)

(1) Percentage was obtained from triangulation method from the product peaks of the G.C. analysis. *Obtained from the integration of the NMR spectra of component A.

(2) Singlet (s), doublet (d), triplet (t), Multiplet (m)

Table 4C NMR Analysis of G.C. Component A,

Chemical Shifts From TMS (δ=0.0)

Product Mixture	(VIIIA)  + (VIIIB) 	
Chemical Shift(δ)	Identification of Proton	
7.4 (s) (10H)	Phenyl Protons	Phenyl protons
6.4-6.7 (m) (1H)		H'_a (J^3=10 Hz)
6.7 to 6.2 (m) (1H)		H'_b (J^4=11 Hz)
5.4 (m) (1H)	H_a	
5.1 (m) (1H)	H_b (J^4=1.7 Hz)	
2.2 (s) (3H)	$-(CH_3)_c$	
1.8 to 2.0 (2d)(3H)		$-(CH_3)'$ (J^3=7 Hz, J^4=1.5 Hz)

Products from the Isomerization of Trans-1-phenyl-2-methyl-cyclopropane (VI) G. C. analysis of the product (6 ft. x ¼ in. 10% SE-30 on 60/80, Chromosorb-P, 130°C) gave three components of retention time at 7.0 min. (A), 9.2 min. (B), and 10.7 min. (C). This three components were collected and purified by preparative G.C. NMR spectra of these three components were obtained for the purpose of identification. NMR analysis of G.C. component A indicated a complicated mixture which was difficult to identify; of component B, which is the major product, indicated the structure of 1-phenyl-2-methylpropene (VIA); and of component C indicated a mixture of cis- and trans-2-phenyl-2-butene (VIB). G.C. analysis of the mixture is listed in Table 5A. The NMR analysis of individual components are listed in Table 5B.

Table 5A: G.C. Analysis of the Product Mixture from the Isomerization Reaction of Compound (VI)

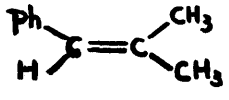
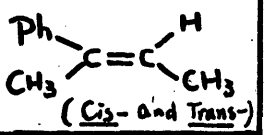
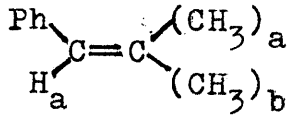
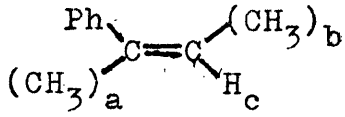
	Component A	(VIA) Component B	(VIB) Component C
Structure	Unable to Identify		 (Cis- and Trans-)
Retention time	7.0 min.	9.2 min.	10.7 min.
Percentage	10.0%	70.0%	20.0%

Table 5B: NMR Analysis of the G.C. Components of the Isomerization of Trans-1-phenyl-2-methylcyclopropane (VI)

G.C. Component B	 (VIA)
Chemical Shifts from TMS (δ=0.0)	Identification of Protons
7.1 (s) (5H)	Phenyl Group
6.2 (m) (1H)	H_a (J^4=1.5 Hz)
1.8 (d) (6H)	$-(CH_3)_a$ and $-(CH_3)_b$ (J^4=1.5 Hz)

G.C. Component C	 (VIB) (cis & trans-)
Chemical Shifts From TMS (δ=0.0)	Identification of Protons
7.3 (s)	Phenyl Group
6.0-6.3 (m)	H_c
2.0 (s)	$-(CH_3)_a$
1.8-1.9 (d)	$-(CH_3)_b$

Product From the Isomerization of trans-1,2-diphenylcyclopropane (IX) The rate of the isomerization of (IX) was found to be twice as fast as that of phenylcyclopropane (VIII). Under G.C. analysis[1], three product components (A,B, and C) were observed. These three components were collected and purified under multiple injections and collection by G.C. NMR spectra were obtained, G.C. analysis of the product mixture is listed in Table 6.

Table 6: G. C. Analysis of Isomerization Product of trans-1,2-diphenylcyclopropane (IX)

	Component A	Component B	Component C
Retention Time	6.5 min.	8.25 min	9.25 min.
Percentage	2.3%	7.5%	90.2%

NMR Analysis of G.C. Components A,B and C From the Isomerization of Compound (IX) The NMR spectra of the G.C. component A and B did not show any information about the structure of Component A and B. The reason may be due to the extremely dilute solution of the sample for running the NMR spectra. G. C. Component C gave a clear

(1) G.C. conditions: 6 ft. x ¼ in. 10% SE-30 on 60/80 Chromosorb-P column of temperature 260°C, with helium as carrier gas at 30 p.s.i. external pressure.

NMR spectrum of δ=7.3 (S), δ=6.2-6.4 (m), δ=3.3 (m) and δ=2.2 (d).

The NMR spectrum of G.C. Component C were difficult to identify, but it indicated the compound is,significantly,not 1,2-diphenylpropene. The Sadtler Standard NMR Spectra Table /15/ indicated the compound is not 2,3-diphenylpropene.

By comparing the NMR spectrum of G.C. Component C to the NMR spectrum of 1,3-diphenylpropene(1), it was found that the chemical shifts and the coupling constants for the protons of these two compounds were identical.

From the above identification, it was concluded that trans-1,2-diphenylcyclopropane(IX) was largely isomerized to 1,3-diphenylpropene.

Product from the Isomerization of cis-1-phenyl-2-methylcyclopropane(V) The rate of isomerization of compound(V) was found to be 0.38 times the rate of phenylcyclopropane(VIII). The reaction had not completed at the time this paper was prepared after 3 months. The NMR analysis indicated the main product from the isomerization of compound(V) was 1-phenyl-2-methylpropene(VIA), which is identical to the main product from trans-1-phenyl-2-methylcyclopropane(VI).

Analysis of the new product peaks of the NMR spectrum of the reaction mixture gave a multiplet (vinyl proton) at δ=6.2 (J^4=1.5 Hz) and two doublets which overlapped at δ=1.7(J^4=1.5Hz).

(1) 1,3-diphenylpropene was prepared from reduction of 1,3-diphenylacetone (Aldrich,Wis.) by sodium borohydride (J.T. Baker, N.J.)/16/ and followed by a dehydration reaction with 85% H_3PO_4 (J.T. Baker, N.J.)/17/.

DISCUSSION

This study generally showed the effect of steric hinderance on the conjugation of the p-orbitals of phenyl to the p-orbitals of cyclopropyl. The proposed mechanism for the isomerization is similar to the suggestion by Roth and Voigt/3/. The relative rates of isomerization of phenylcyclopropane (VIII), cis-1-phenyl-2-methylcyclopropane(V), trans-1-phenyl-2-methylcyclopropane(VI), trans-1,2-diphenylcyclopropane(IX) and 1-phenyl-1-methylcyclopropane(VII) are compared below.

Rate Expression of the Isomerization Reaction. The rate of isomerization of phenylcyclopropane(VIII) was deduced and calculated from the integrations of the NMR spectra. A plot of the concentration of (VIII) with respect to time is given in Figure 6. The result of this graph indicates a zero order reaction for compound (VIII) when the concentration of compound (VIII) is greater than 5.65×10^{-4} mmole. The rate constant (which is the slope of the line), expressed by $-d[(VIII)]/d(time)$ is found to be 7.01×10^{-2} mmole/day. The rate of the isomerization reaction decreases when the concentration of the substrate (compound VIII) is smaller than 5.65×10^{-4} mmole. This change may be caused by the diffusion effect of the substrate in a very dilute solution. The accuracy of the calculation of the concentration of substrate from the integrations of NMR spectra was estimated to be $\pm 5\%$.

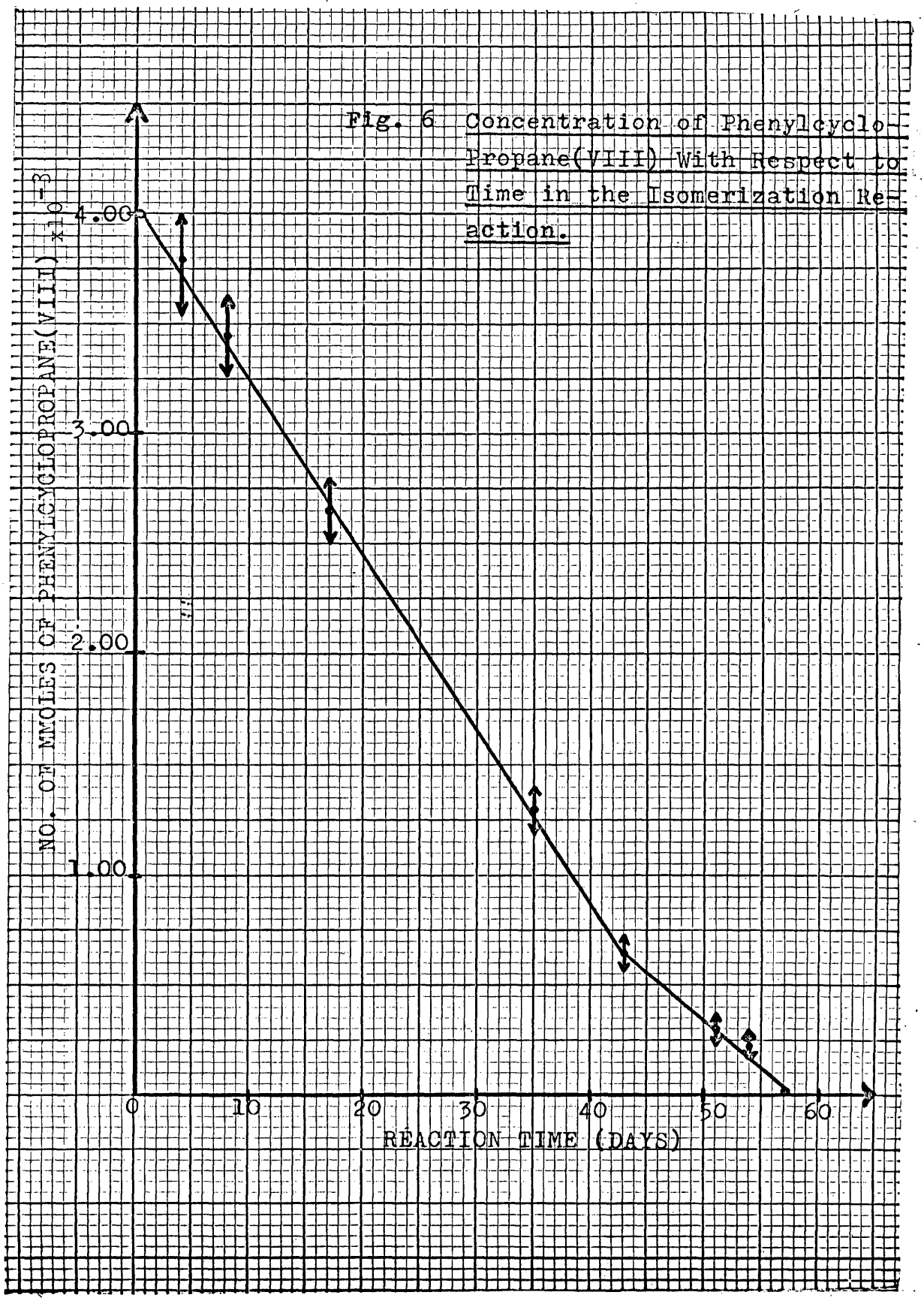


Fig. 6 Concentration of Phenylcyclo-Propane(VIII) With Respect to Time in the Isomerization Reaction.

The Nature of the Substrate.

The M.O. Orbital Diagram of the Phenylcyclopropanes.

The M.O. diagrams of cyclopropane and conjugated vinylcyclopropane were proposed by Pasto, Chen and Binsch (fig.4)/6/. In the phenylcyclopropanes system, the "π-type" molecular orbital, for the p-orbital of the phenyl conjugated with the p-orbital of the cyclopropyl, is illustrated in Figure 7.

It is obvious that, from studying Figure 7, the plane of the phenyl group must bisect the plane of the cyclopropyl ring in order to allow the p-orbital of the phenyl ring to conjugate with the cyclopropyl p-orbital, to gain the most stable conformation.

However, if R_1 or R_2 is a methyl group, steric hinderance will inhibit conjugation of the phenyl group. As a result, the phenyl group is no longer able to assume this stable arrangement. This inhibition affects the rate of the reaction significantly (discussed in next section).

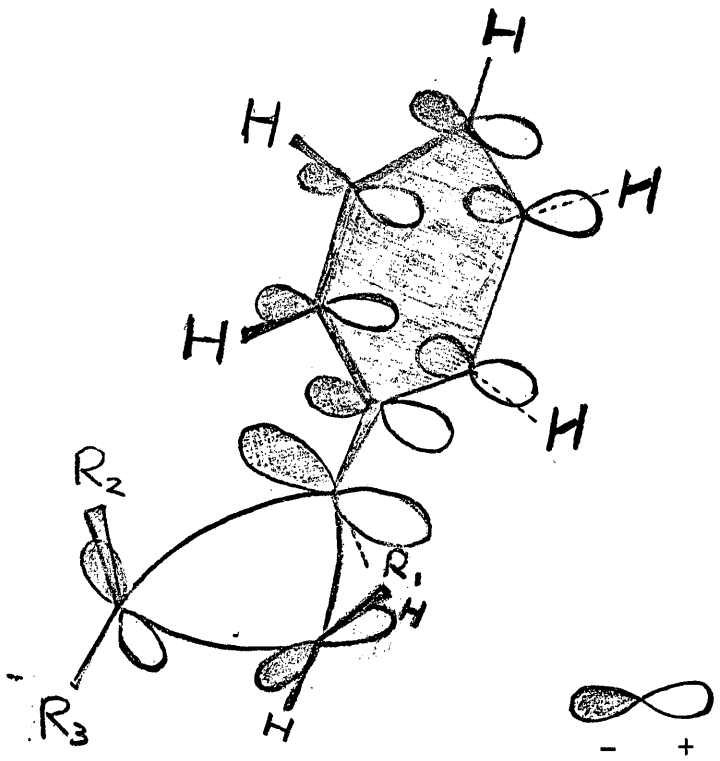


Fig. 7 The Side View of the MO. of phenylcyclopropane in which the π-electron of the phenyl group is conjugated with the p-orbital of the cyclopropyl ring

(VIII)	R_1= H ,	R_2= H ,	R_3= H
(VII)	R_1= $-CH_3$,	R_2= H ,	R_3= H
(V)	R_1= H ,	R_2= $-CH_3$,	R_3= H
(VI)	R_1= H ,	R_2= H ,	R_3= $-CH_3$
(IX)	R_1= H	R_2= H ,	R_3= -Ph

Steric Effect: The Dependence of Reaction Rate on Structure. According to Roth and Voigt/3/, the structural features of cyclopropane that can influence this isomerization reaction are limited to those in which there is conjugation of a phenyl group or a vinyl group with the cyclopropyl ring. In such cases, the preferable conformation of the phenyl group of the phenylcyclopropane, which is active to this catalytic reaction (as discussed in the last section) must be kept in a position wherein the phenyl group is bisecting the cyclopropyl ring.

The rate of the isomerization reaction, as shown in Table 3, was found to be trans-1-phenyl-2-methyl-cyclopropane (VI)>>trans-1,2-diphenylcyclopropane(IX)>phenylcyclopropane (VIII)>cis-1-phenyl-2-methylcyclopropane (V)>>1-phenyl-1-methylcyclopropane (VII).

In compound (VII), the steric hinderance between the phenyl group and the methyl group is so large that the phenyl group is forced completely out of the preferred conjugated position. As a result, the π-electron of the phenyl group can no longer delocalize to the p-orbital of the cyclopropyl ring and compound (VII) was found to be inactive in the catalytic isomerization reaction.

Similarly, the phenyl group of compound(V) is forced out of the preferred conjugated arrangement, but, in this

compound, the steric hinderance between the phenyl and the methyl group is not as large as that of compound (VII). This arrangement allows the rate of isomerization to be 0.38 times that of compound (VIII).

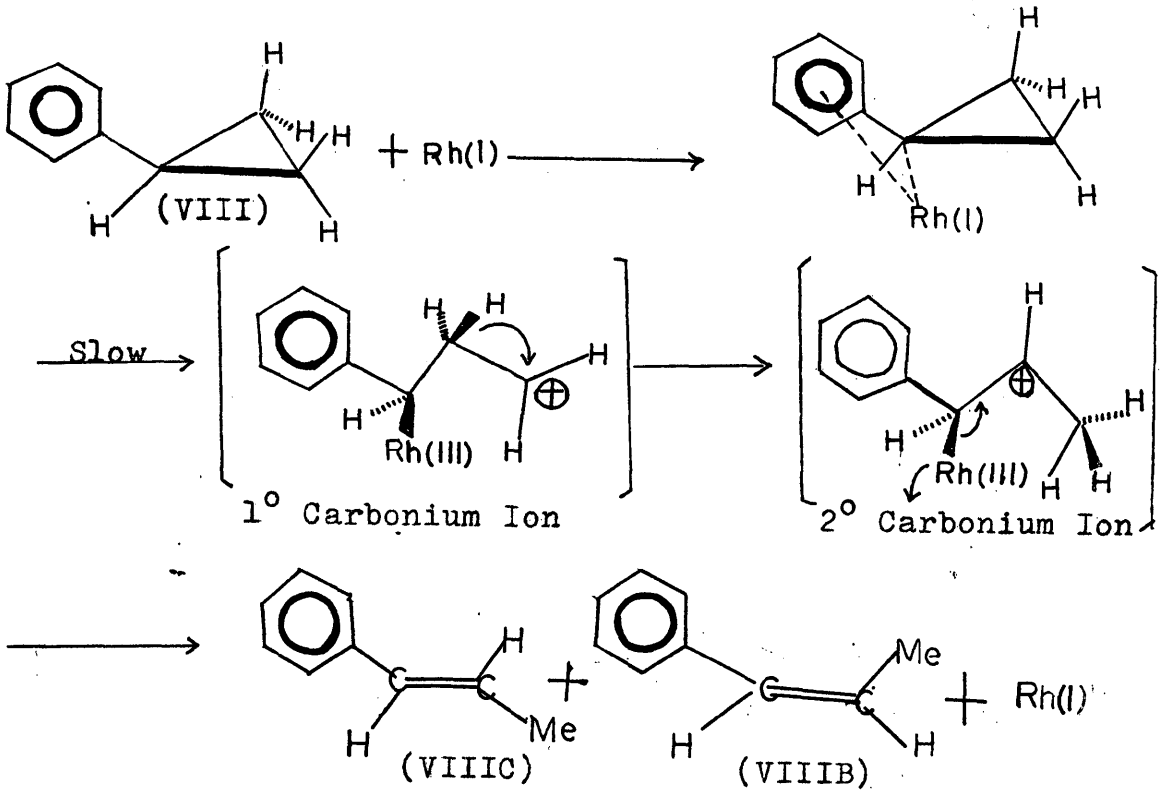
In both compound (VI) and compound (IX), no steric hinderance between the phenyl group and the methyl group or the two phenyl groups, respectively, can be detected. As a matter of fact, the rate of isomerization of compound (IX) is 2.03 times the rate of compound (VIII) and compound (VI) is 13.5 times that of compound (VIII).

The increase in rate of compound (IX) may be a statistical result because, in this compound, two phenyl groups are in the same relation to the cyclopropyl. The chance of being attacked by the catalyst is twice that of the phenylcyclopropane.

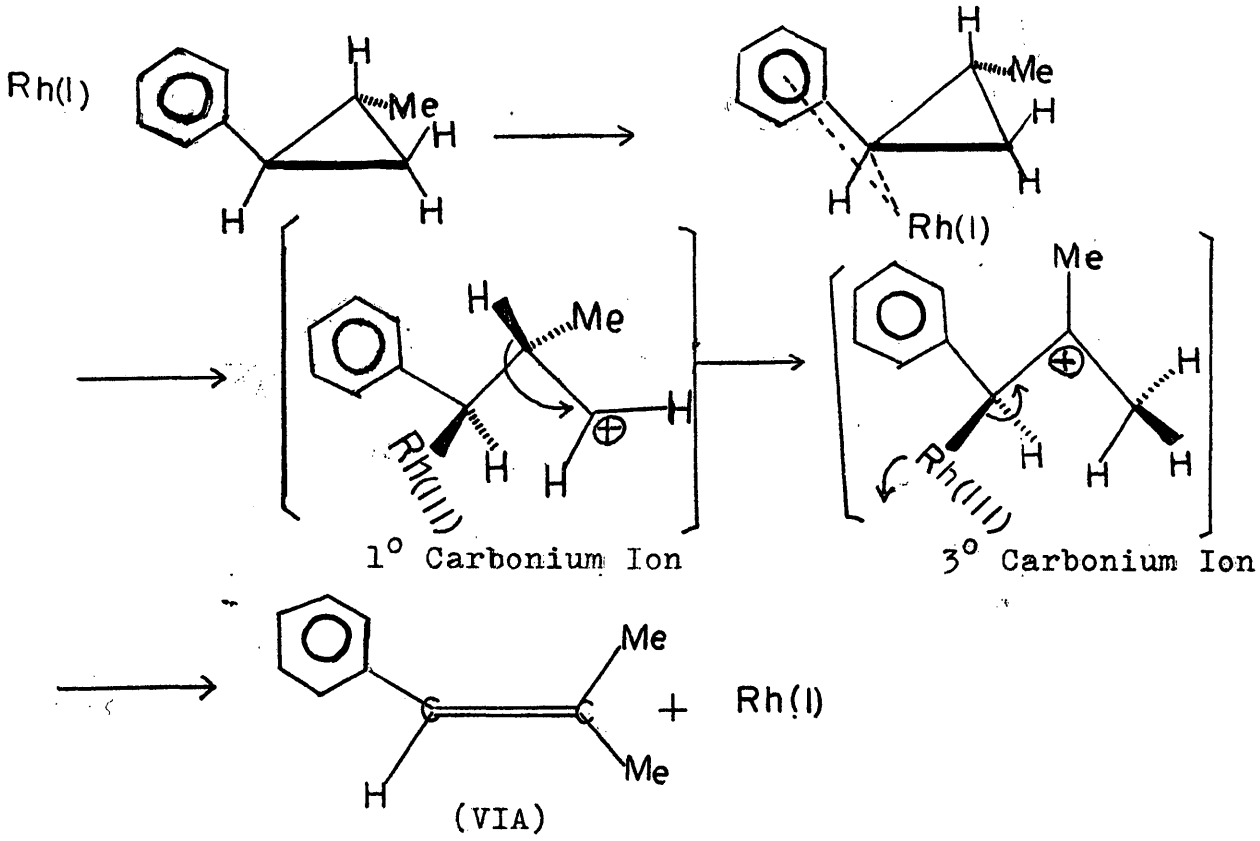
The rate of isomerization of compound (VI) was found to be very much faster than the rate of phenylcyclopropane (VIII). This effect may be due to the increased stability of the carbonium ion intermediates which are discussed below.

Proposed Mechanism of the Isomerization Reaction: Formation of Carbonium ion as Intermediate. According to Roth and Voigt/3/, the intermediate in the isomerization reaction of vinylcyclopropane may be a carbonium ion, followed by a 1,2-hydride transformation. In the case of phenylcyclopropane (VIII), the ring opening of the cyclopropyl is in the

carbon-carbon bonds closer to the phenyl group. The mechanism is suggested as in the following illustration.



For the isomerization of trans-1-phenyl-2-methyl-cyclopropane(VI), according to the suggested mechanism, a 3^{o} carbonium ion was formed. The rate of isomerization of compound (VI) should be faster than that of phenylcyclopropane(VIII) due to the stability of the 3^{o} carbonium ion. The rate of isomerization of compound (VI) was found to be 13.5 times the rate of compound (VIII), and therefore, is not surprising. The ring-opening occurred at the carbon-carbon bond of the cyclopropyl across the ring from the methyl group. The mechanism of the isomerization of compound (VI) is suggested as in the following illustration.



NMR Spectra Related to the Conjugation of the Phenyl with Cyclopropyl of the Substrates. The NMR spectra of phenylcyclopropane(VIII), trans-1-phenyl-2-methylcyclopropane (VI) and trans-1,2-diphenylcyclopropane(IX) showed that

the phenyl protons are split into a multiplet(1). This NMR pattern suggests that the phenyl group in these compounds is in a preferred conjugated arrangement and is not a freely rotating group. In this arrangement a multiplet should be found for the phenyl protons' spectra because the protons of the phenyl group are not in equivalent magnetic envorments.

For the spectrum of cis-1-phenyl-2-methylcyclopropane (V) and 1-phenyl-1-methylcyclopropane (VII), a sharp singlet for the phenyl protons was observed(2). Free rotation of the phenyl group, not conjugated to the cyclopropyl, is suggested by this observation.

The above argument was based on the interpretation of the NMR spectra of styrene/18/, 3-phenylpropene and iso-propylbenzene/19/. The phenyl protons of styrene split into a multiplet because of the conjugation of the p-orbitals of the phenyl to the p-orbital of the carbon-carbon double bond, thus the phenyl group in styrene is not freely rotated. A sharp singlet for the NMR spectrum of the phenyl group of 3-phenylpropene and iso-propyl-benzene is observed. In these compounds, the phenyl group is freely rotating because there is no available p-orbital

(1) Refer to Appendix 3A, 6A and 10A respectively.

(2) Refer to Appendix 7A and 1B

that can conjugate with the phenyl p-orbital. The NMR spectrum of the phenyl groups of 3-phenylpropene, styrene and iso-propylbenzene are listed in Figure 8.

Nature of Product

The isomerization of phenylcyclopropane (VIII) yields 50% of trans-β-methylstyrene (VIIIC), 30% of cis-propenylbenzene (VIIIB) and compound (VIIIC) are the two predicted products from the proposed mechanism of the isomerization. It is not surprising that (VIIIC) is the predominant product because, thermodynamically, (VIIIC) is the more stable isomer. The intermediate produced from (VIII), which may be a freely rotating carbonium ion, will prefer a conformation that gives (VIIIC) as the major product.

Surprisingly, 20% of α-methylstyrene was obtained as a minor product from the isomerization of (VIII). This result indicates that more than one mode of ring opening is possible and although this mode is not predominant, it is allowed. The mechanism for this less favored mode of ring opening, which gives 20% of α-methylstyrene (VIIIA) as an isomerization product of compound (VIII), is illustrated in the following diagram.

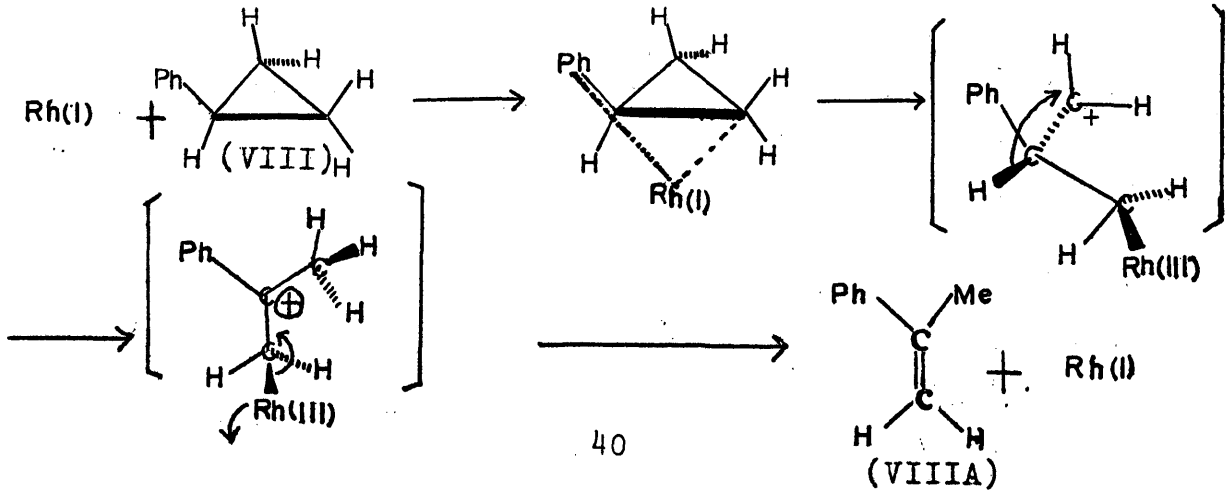
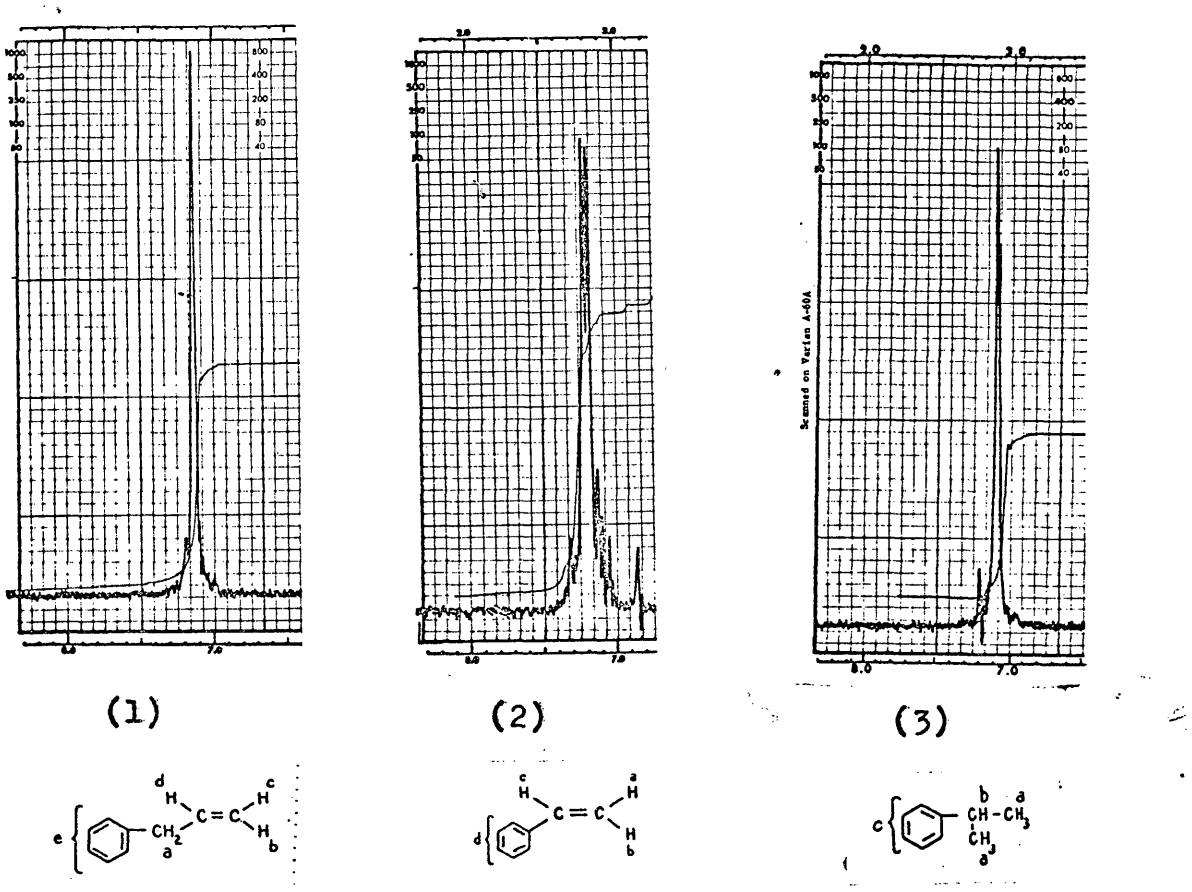
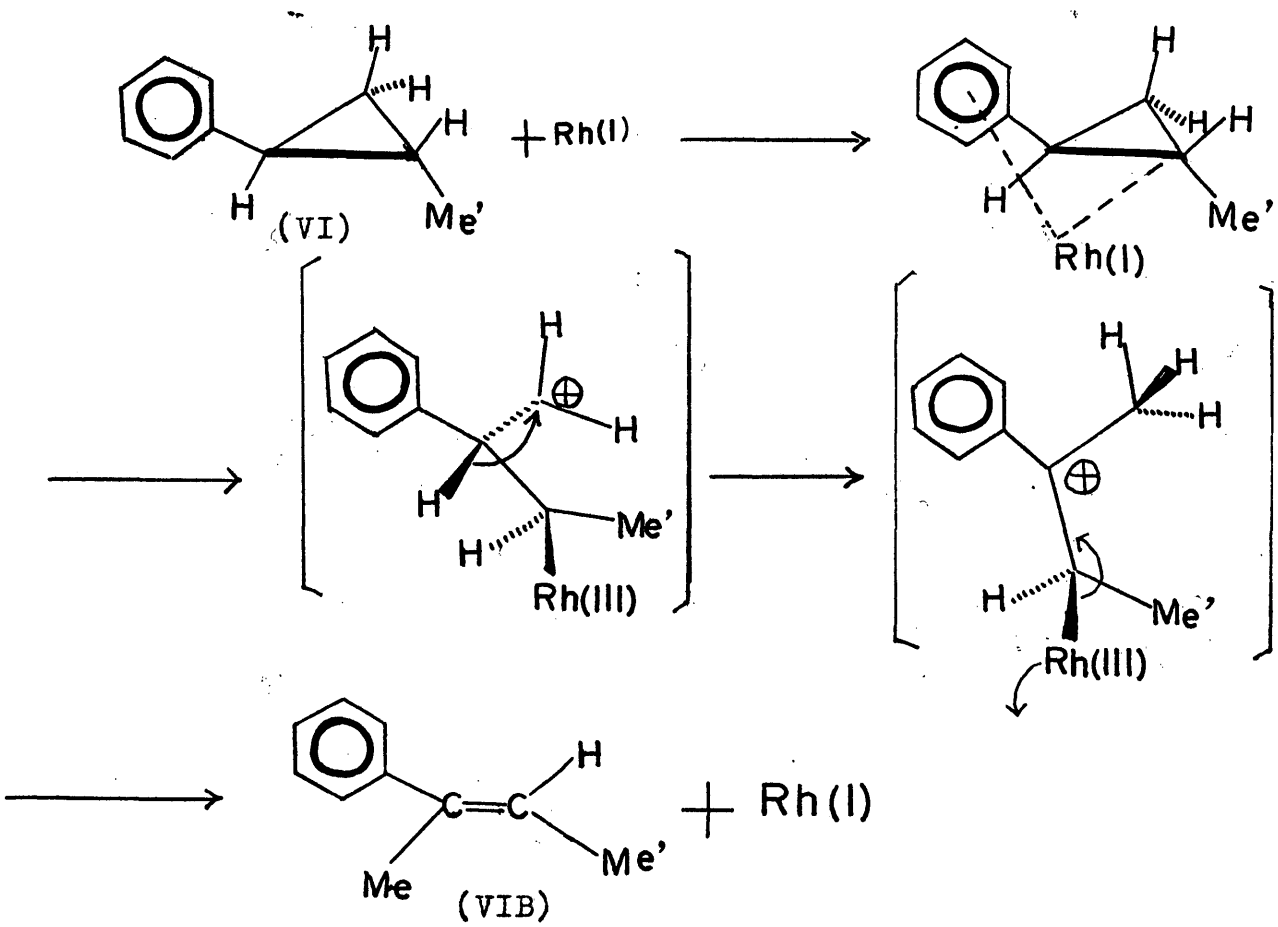


Figure 8 : The NMR Spectra of the Phenyl Group of 3-phenylpropene(1), Styrene(2) and Iso-propylbenzene(3)



(1) Sadtler NMR Table No. 3248 (1972)
(2) Sadtler NMR Table No. 6480 (1972)
(3) Sadtler NMR Table No.10183 (1972)

Isomerization of trans-1-phenyl-2-methylcyclopropane (VI) and cis-1-phenyl-2-methylcyclopropane(V) gave a major product of 1-phenyl-2-methylpropene(VIA) as predicted by the proposed mechanism. For compound (VI), 70% of (VIA) was obtained. It is not surprising, in referring to the isomerization of phenylcyclopropane(VIII), that 20% of cis- and trans-1-methyl-2-phenylpropene were products from the isomerization of compound (VI). This result again indicates there is more than one mode of allowed ring opening, as illustrated in the following diagram.

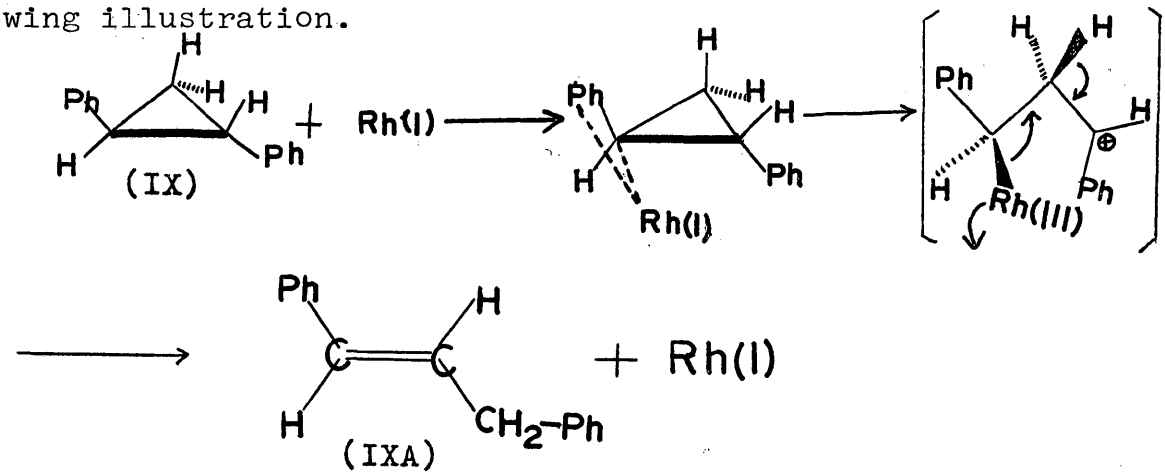


Cis- and Trans-

The last 10% of the isomerization products[1] (G.C. component A) of compound (VI) were difficult to identify by the NMR spectra.

It is not surprising that trans-1-phenyl-2-methyl-cyclopropane (VI) and cis-1-phenyl-2-methylcyclopropane(V) have the same main product from the isomerization reaction because, according to the proposed mechanism, compound (V) and compound (VI) should have the same carbonium ion intermediate.

Isomerization of trans-1,2-diphenylcyclopropane(IX) quantitatively gives a product of 1,3-diphenylpropene(IXA). The suggested mode of ring-opening is in the carbon-carbon bond of cyclopropyl between the two phenyl groups. The mechanism of the isomerization reaction may be as in the following illustration.



Apparently, no allylbenzene was formed in the isomerization reactions. All products are conjugated vinylbenzenes.

(1) According to the complicated NMR spectrum of this isomer, this 10% of product could be a mixture of polymers.

Nature of Catalyst. $[Rh(CO)_2Cl]_2$ has been reported not to be an efficient catalyst for low pressure hydrogenation of α-cyclopropylstyrene/20/. Instead of obtaining the hydrogenated product, the reaction gave only the product of isomerization from the ring opening of the cyclopropyl. This observation may indicate that Rh(I) formed a coordination complex with cyclopropylalkene and phenylcyclopropane.

Apparently, coordination of Rh(I) with the conjugated cyclopropane must take place in the less sterically hindered position because of the large ionic radius of the rhodium metal. This result is reflected by the products obtained from the isomerization of trans-1-phenyl-2-methylcyclopropane (VI) and cis-1-phenyl-2-methylcyclopropane(V), as indicated by the proposed mechanism.

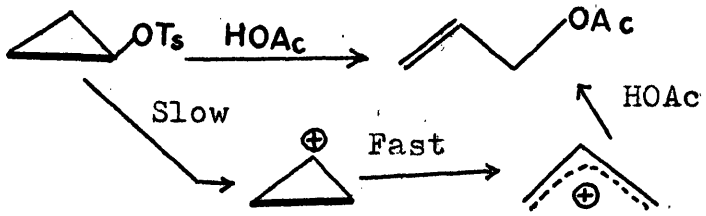
CONCLUSION

This study has established that the phenylcyclopropanes may undergo homogeneous isomerization, in the presence of catalytic amount of $[Rh(CO)_2Cl]_2$, to yield isomeric products, provided that the p-electrons of the phenyl group can delocalize to the p-orbitals of cyclopropyl. The ability of the phenyl group to conjugate with cyclopropyl is governed by steric effects and thus, determines the rate of the isomerization. The intermediate of the isomerization is suggested to be a carbonium ion. The similarity of the products from compound (V) and compound (VI) indicate a common intermediate is formed, probably a carbonium ion formed in the oxidation-reduction reaction with rhodium. The stability of the intermediate carbonium ion is thought to have an influence on the rate and kind of the isomerization. Conjugation of the phenyl to the cyclopropyl was the principle determinant. The configuration of the isomerization product was found to be the one which is the thermodynamically most stable one.

The mechanism of the coordination of the substrate to the Rh(I) is not well defined. Rh(I) was reported to be oxidized to Rh(III) during the ring-opening of the cyclopropyl/3/. All evidence from the result of the isomerization indicates the possibility of the formation of carbonium ion intermediates.

According to the major product from the isomerization of phenylcyclopropane(VIII) (50% trans-β-methylstyrene) and the work done by Radom and Pople/9/, it is suggested that the carbonium ion intermediate from ring-opening of cyclopropyl ring may not be an allyl-type carbonium ion because of the higher relative energy of allyl-type carbonium ion in comparison to the classical carbonium ion.

From the study of cyclopropyl solvolyses by Sliwinski, Su and Schleyer/21, 22/, an allyl cation () was proposed to be the intermediate of the ring opening reaction as illustrated in the following.



According to the above arguments, more research work is needed to establish the mechanism of formation of the carbonium ion in the ring-opening reaction of cyclopropane.

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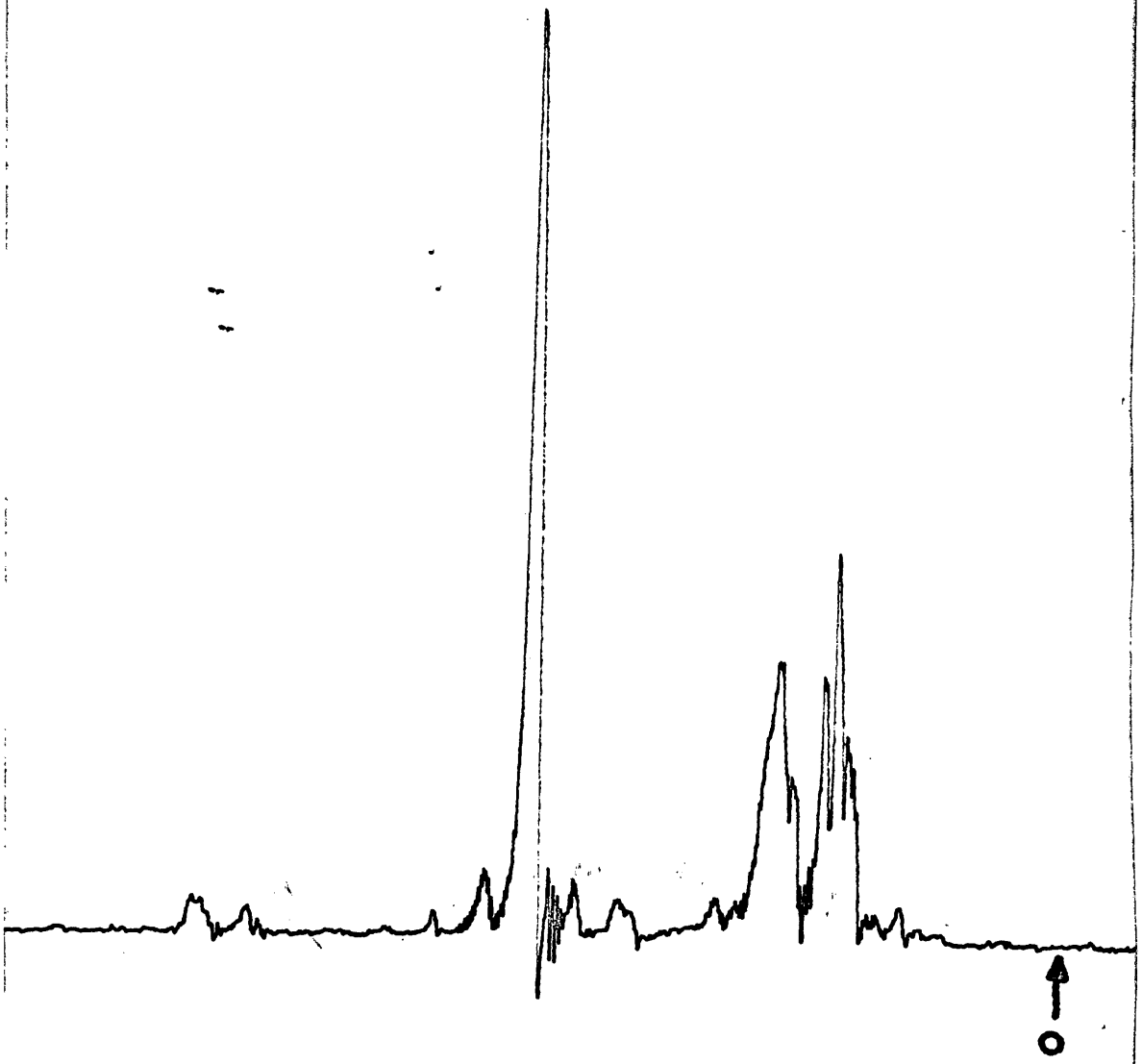
1A. Kinetic Data for Isomerization Reaction of (VII)

NMR Spectrum of (VII) at time = 0.0 day

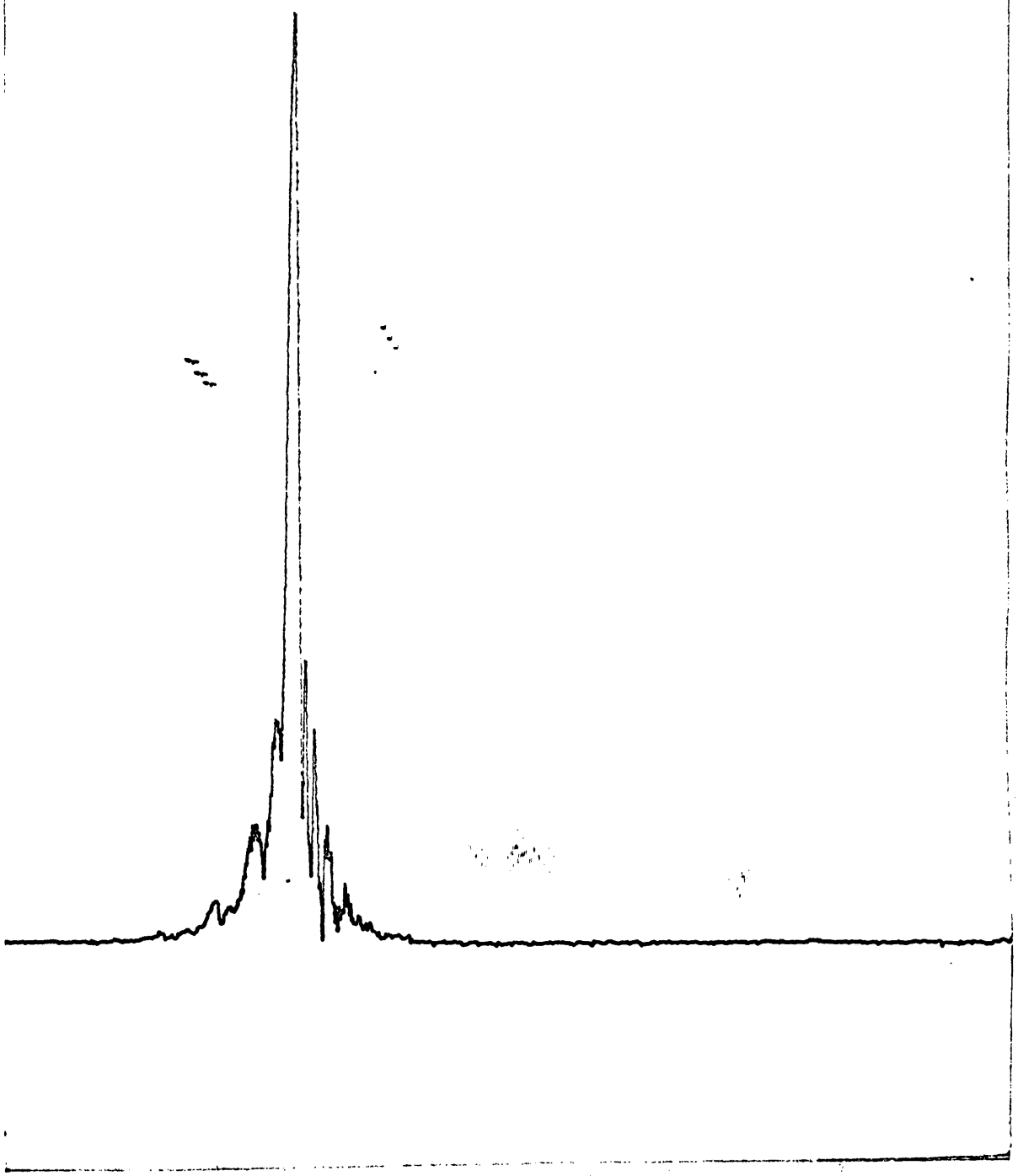
(0. Hz to 160 Hz)



1B. Kinetic Data for Isomerization Reaction of (VII)

NMR Spectrum of (VII) at time = 0.0 day

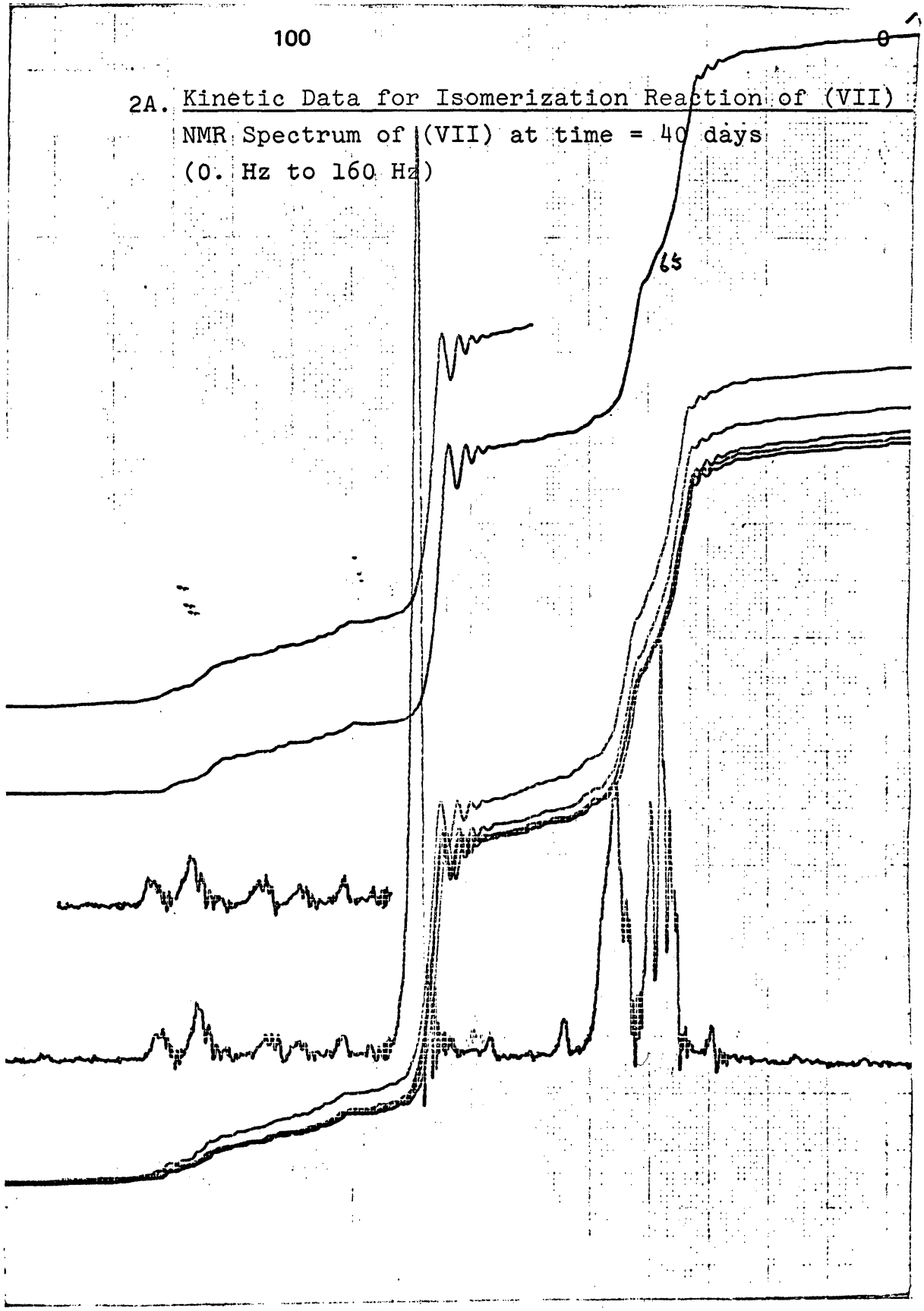
(330 Hz to 500 Hz)



2A. Kinetic Data for Isomerization Reaction of (VII)

NMR Spectrum of (VII) at time = 40 days

(0. Hz to 160 Hz)

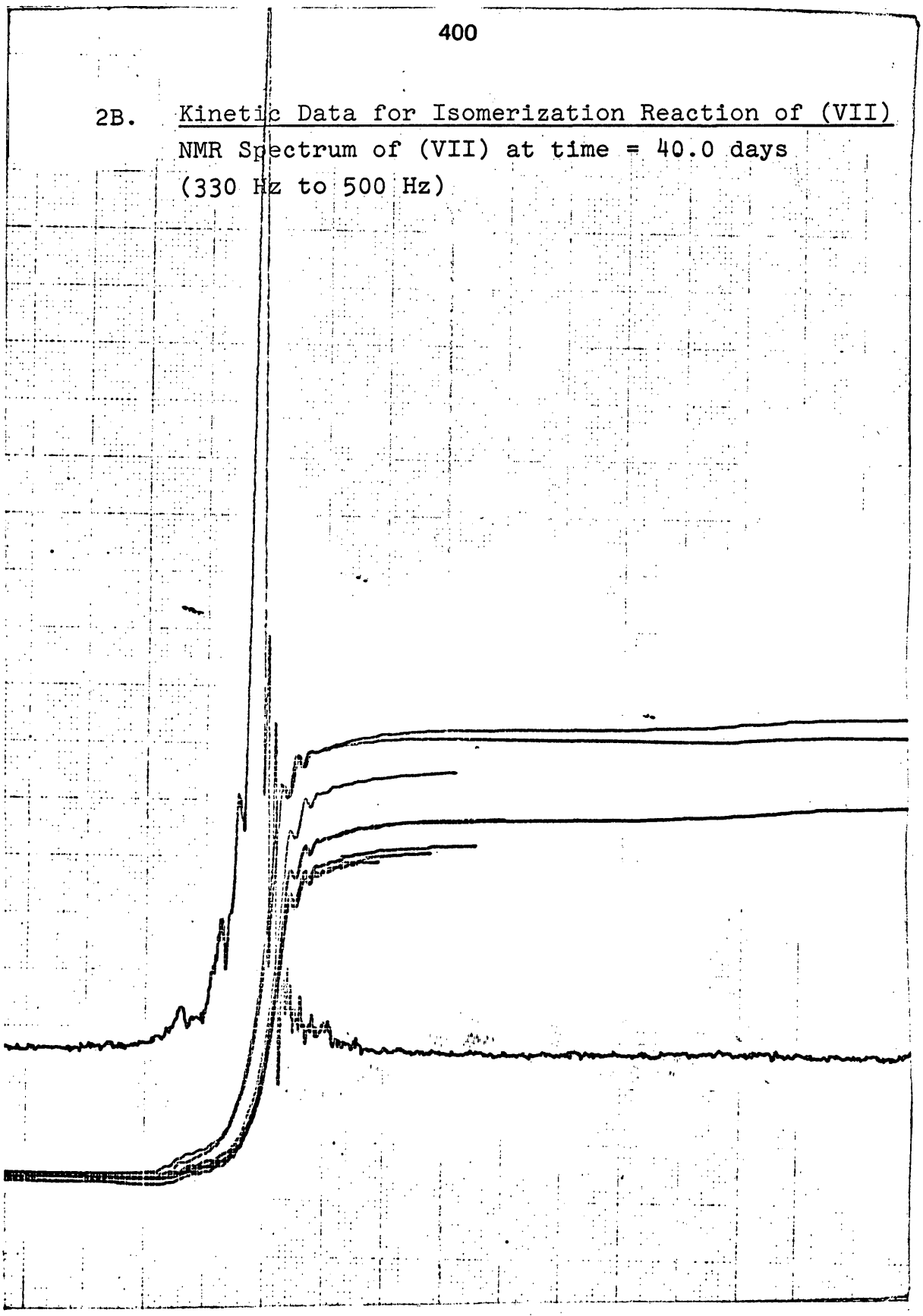


400

2B. Kinetic Data for Isomerization Reaction of (VII)

NMR Spectrum of (VII) at time = 40.0 days

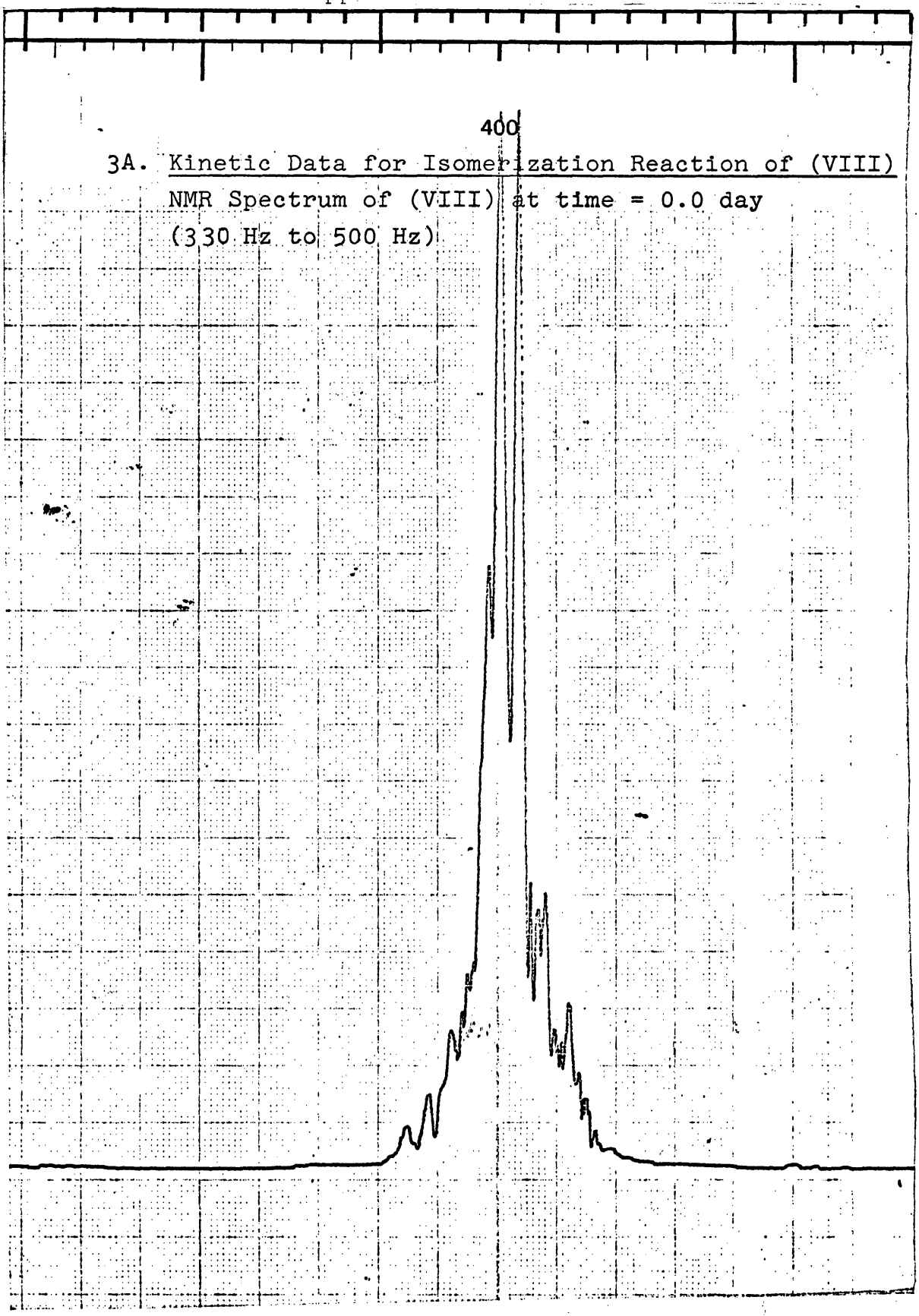
(330 Hz to 500 Hz)



3A. Kinetic Data for Isomerization Reaction of (VIII)

NMR Spectrum of (VIII) at time = 0.0 day

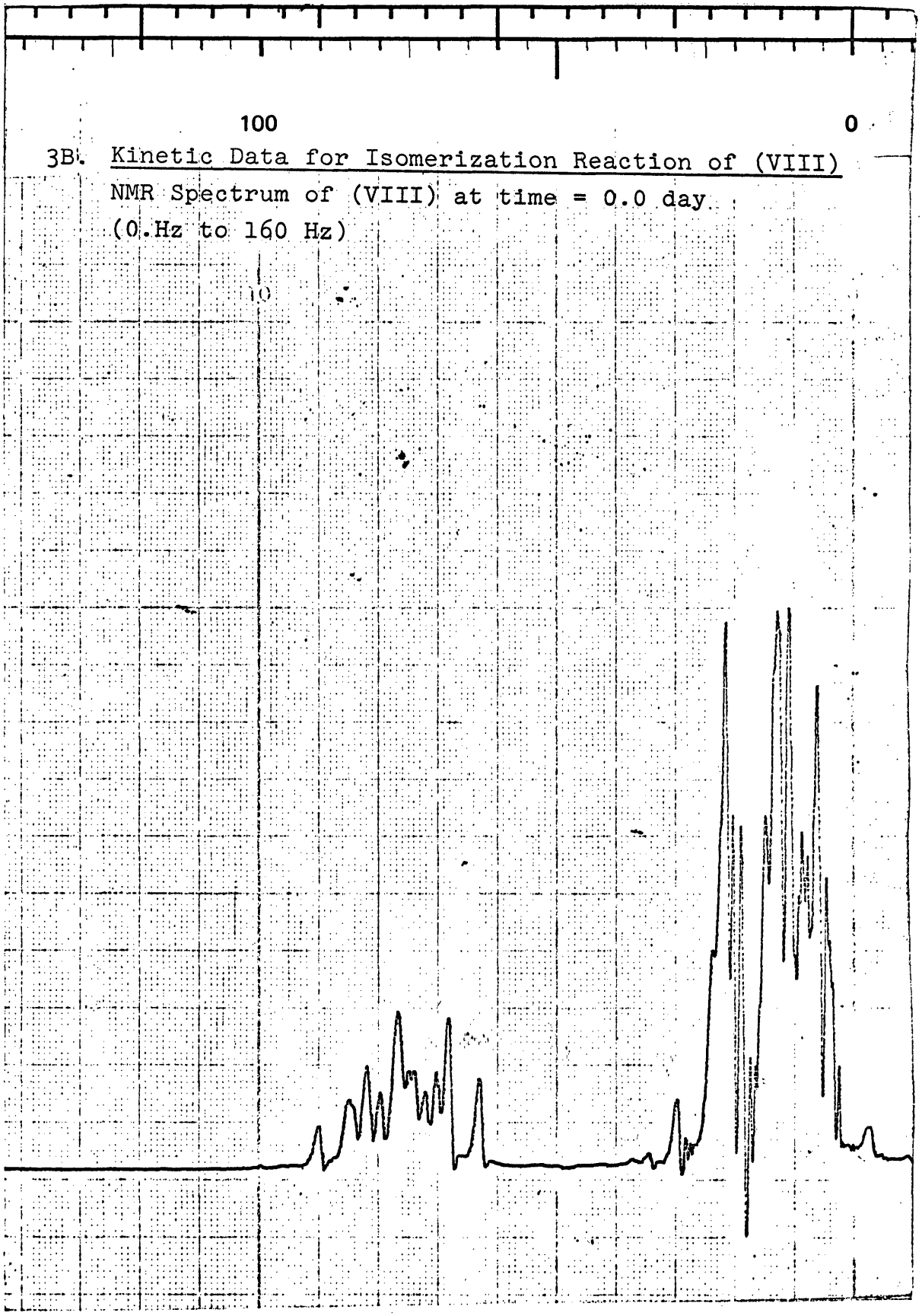
(330 Hz to 500 Hz)

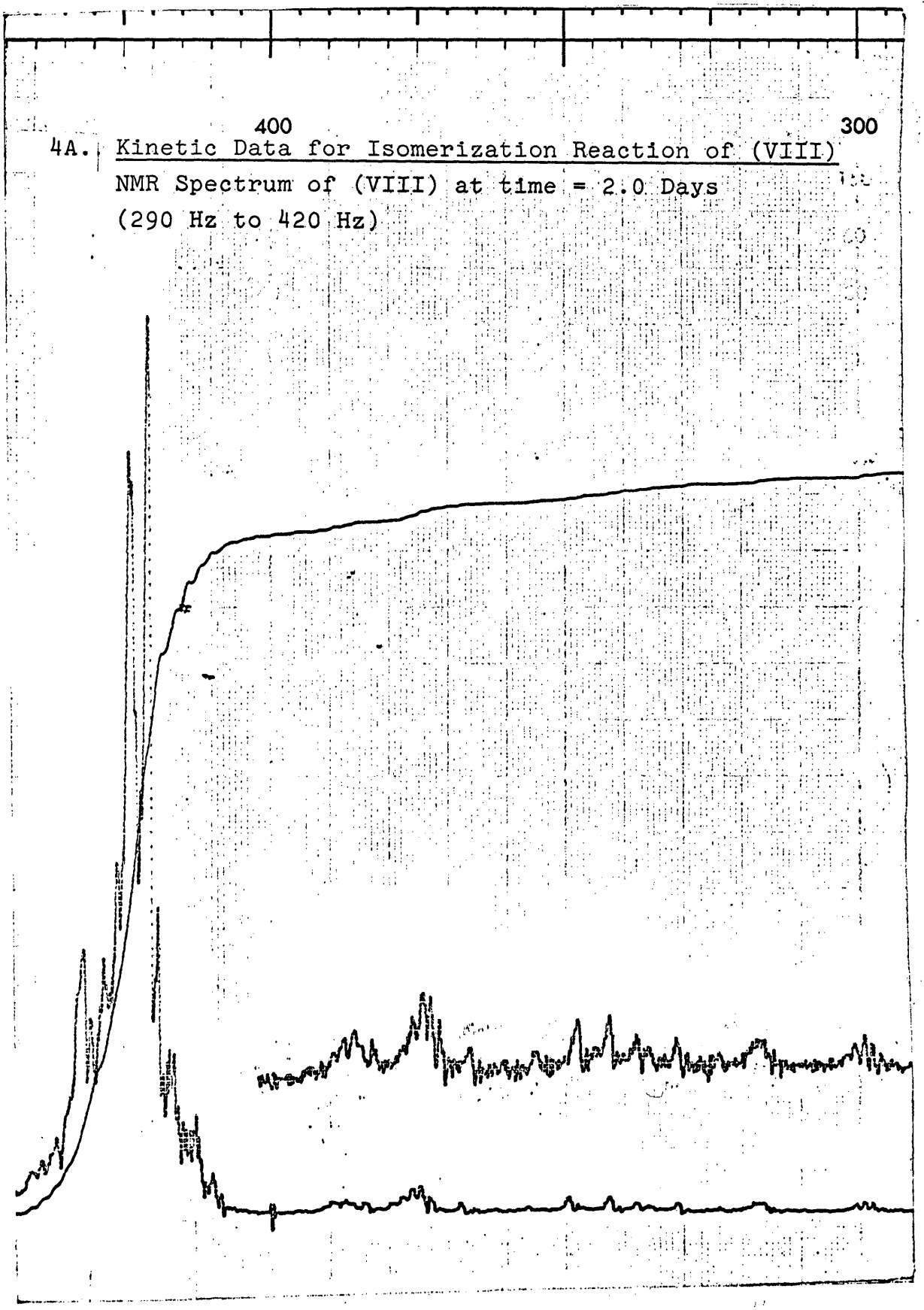


3B. Kinetic Data for Isomerization Reaction of (VIII)

NMR Spectrum of (VIII) at time = 0.0 day

(0.Hz to 160 Hz)

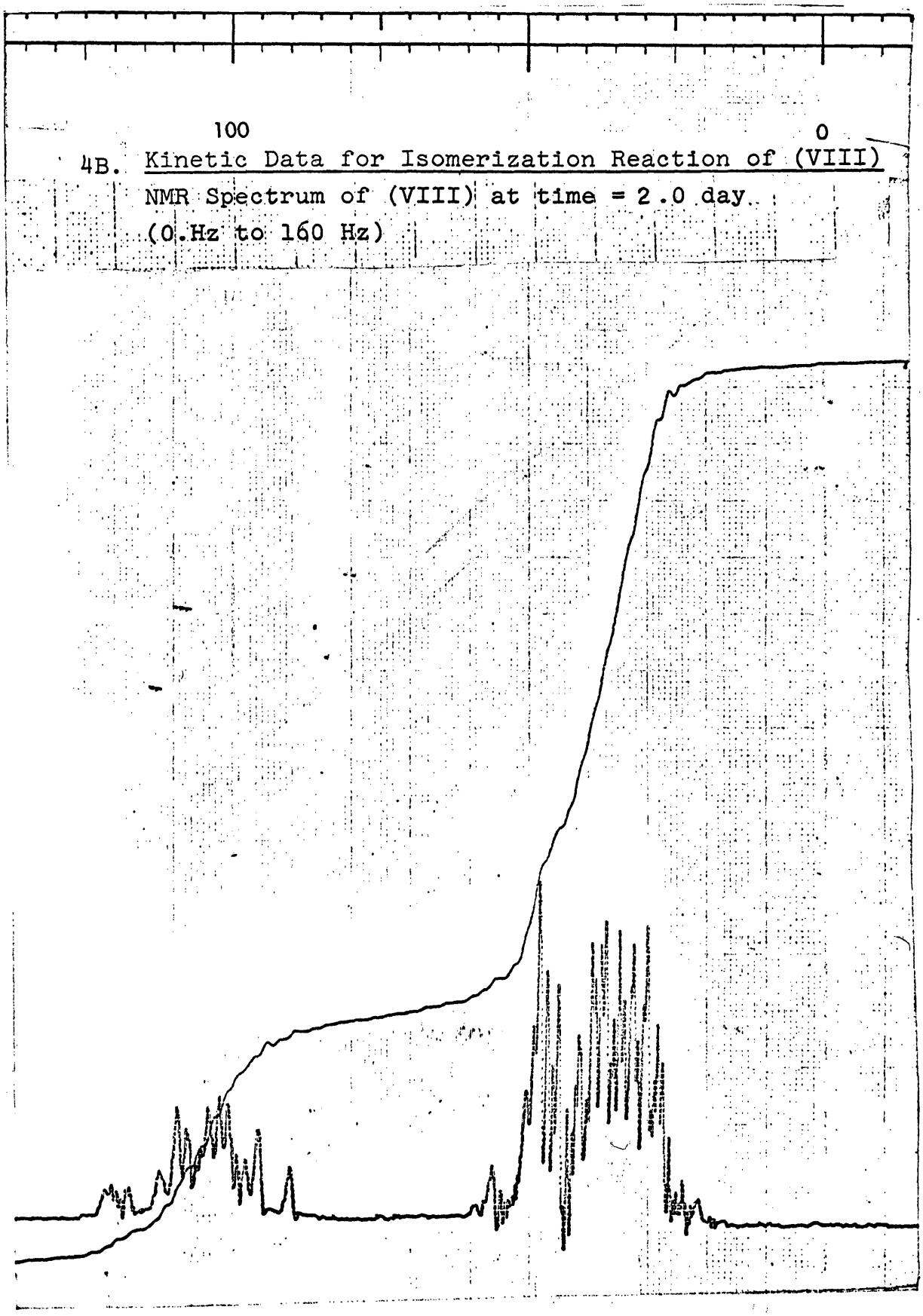




4A. Kinetic Data for Isomerization Reaction of (VIII)

NMR Spectrum of (VIII) at time = 2.0 Days

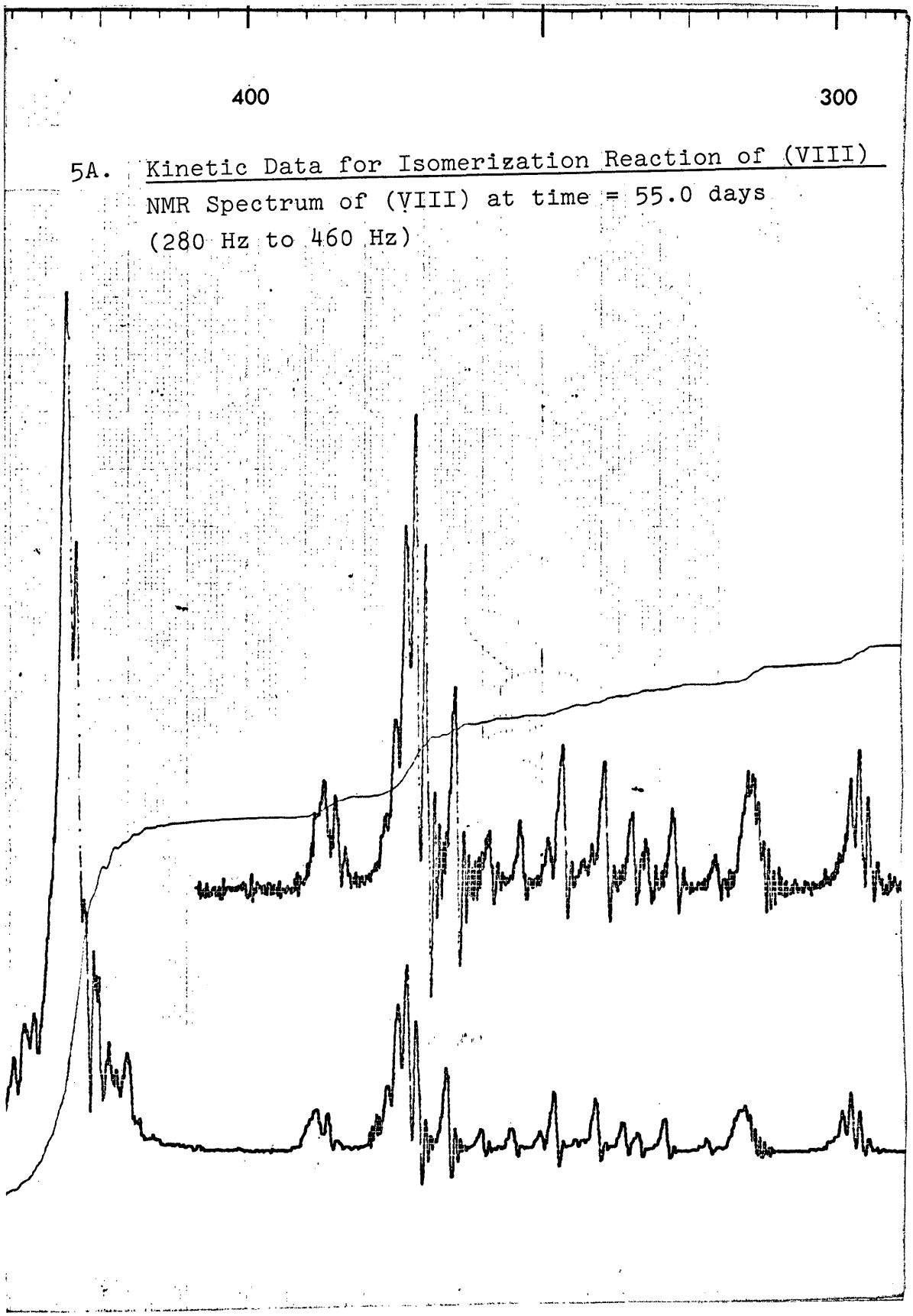
(290 Hz to 420 Hz)



4B. Kinetic Data for Isomerization Reaction of (VIII)

NMR Spectrum of (VIII) at time = 2.0 day

(0 Hz to 160 Hz)



5A. Kinetic Data for Isomerization Reaction of (VIII)

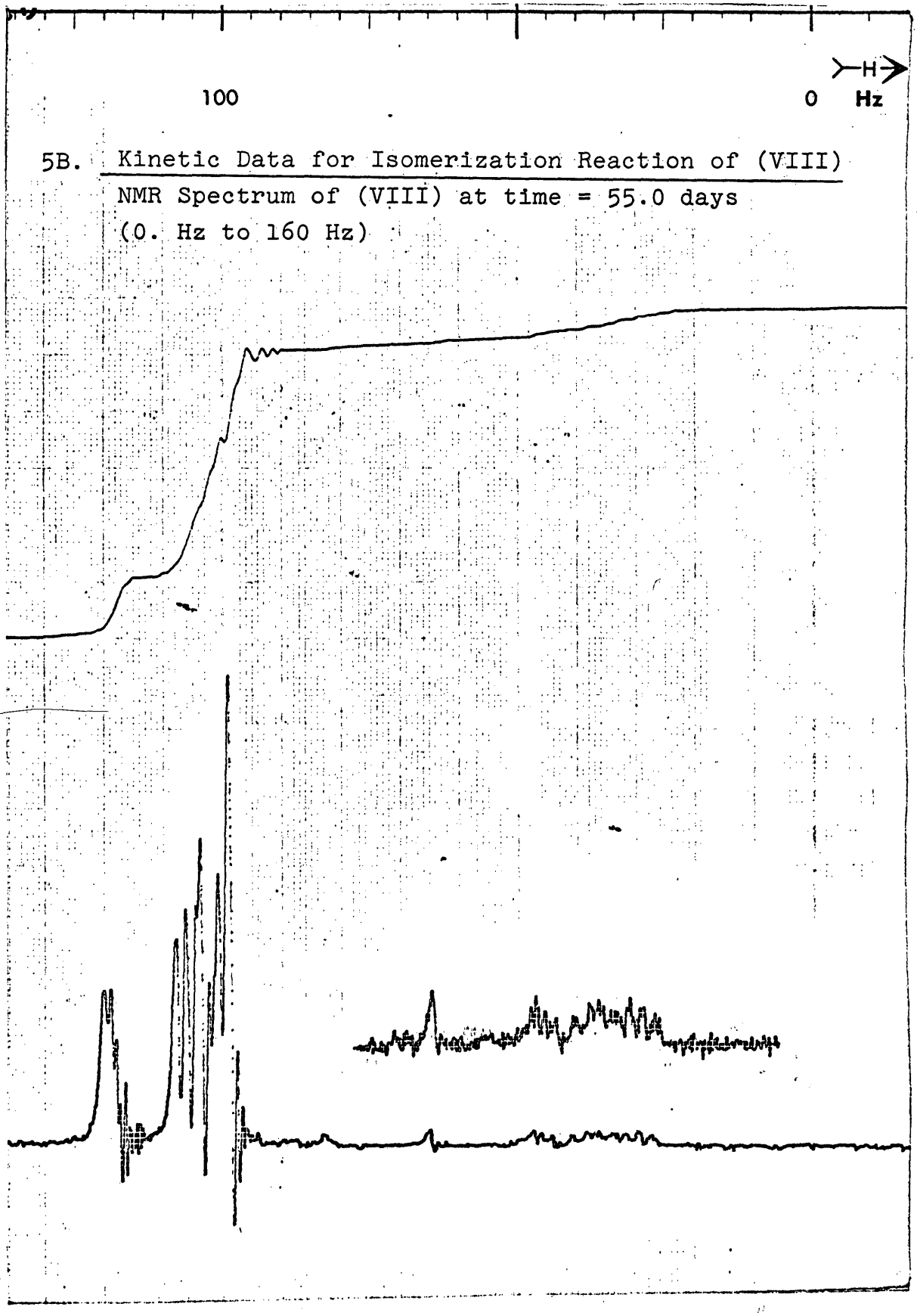
NMR Spectrum of (VIII) at time = 55.0 days

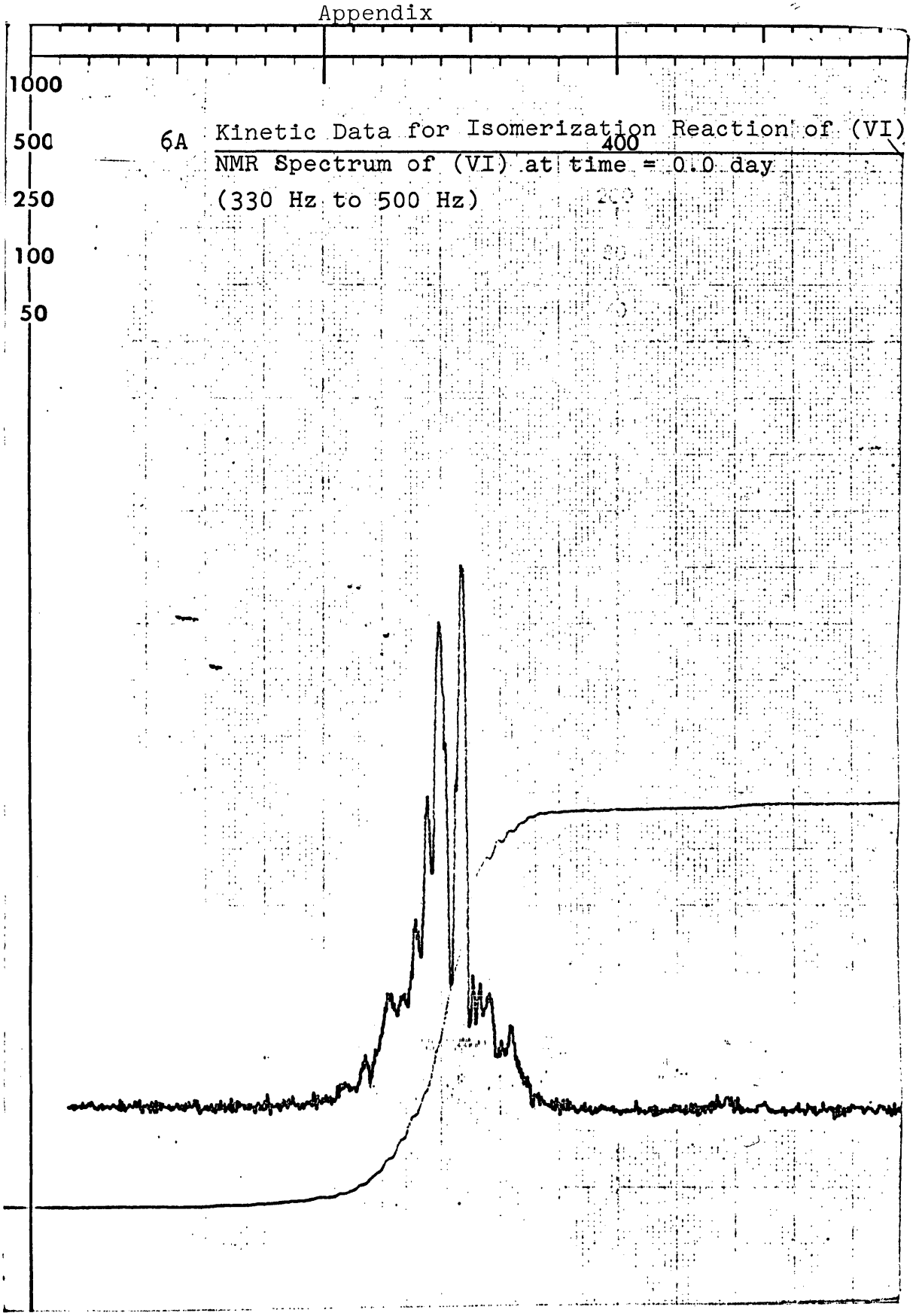
(280 Hz to 460 Hz)

5B. Kinetic Data for Isomerization Reaction of (VIII)

NMR Spectrum of (VIII) at time = 55.0 days

(0. Hz to 160 Hz)





6A Kinetic Data for Isomerization Reaction of (VI)

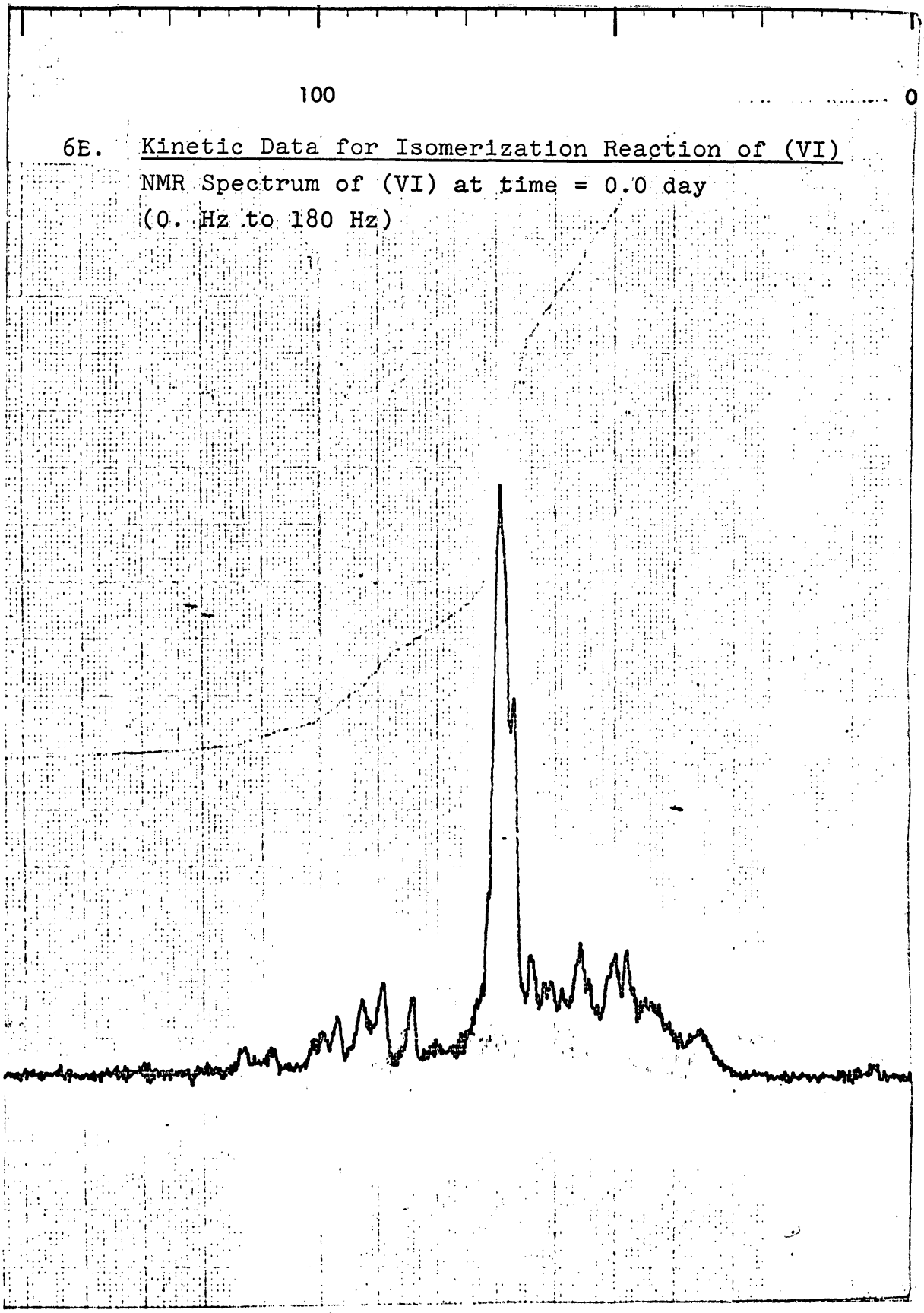
NMR Spectrum of (VI) at time = 0.0 day

(330 Hz to 500 Hz)

6E. Kinetic Data for Isomerization Reaction of (VI)

NMR Spectrum of (VI) at time = 0.0 day

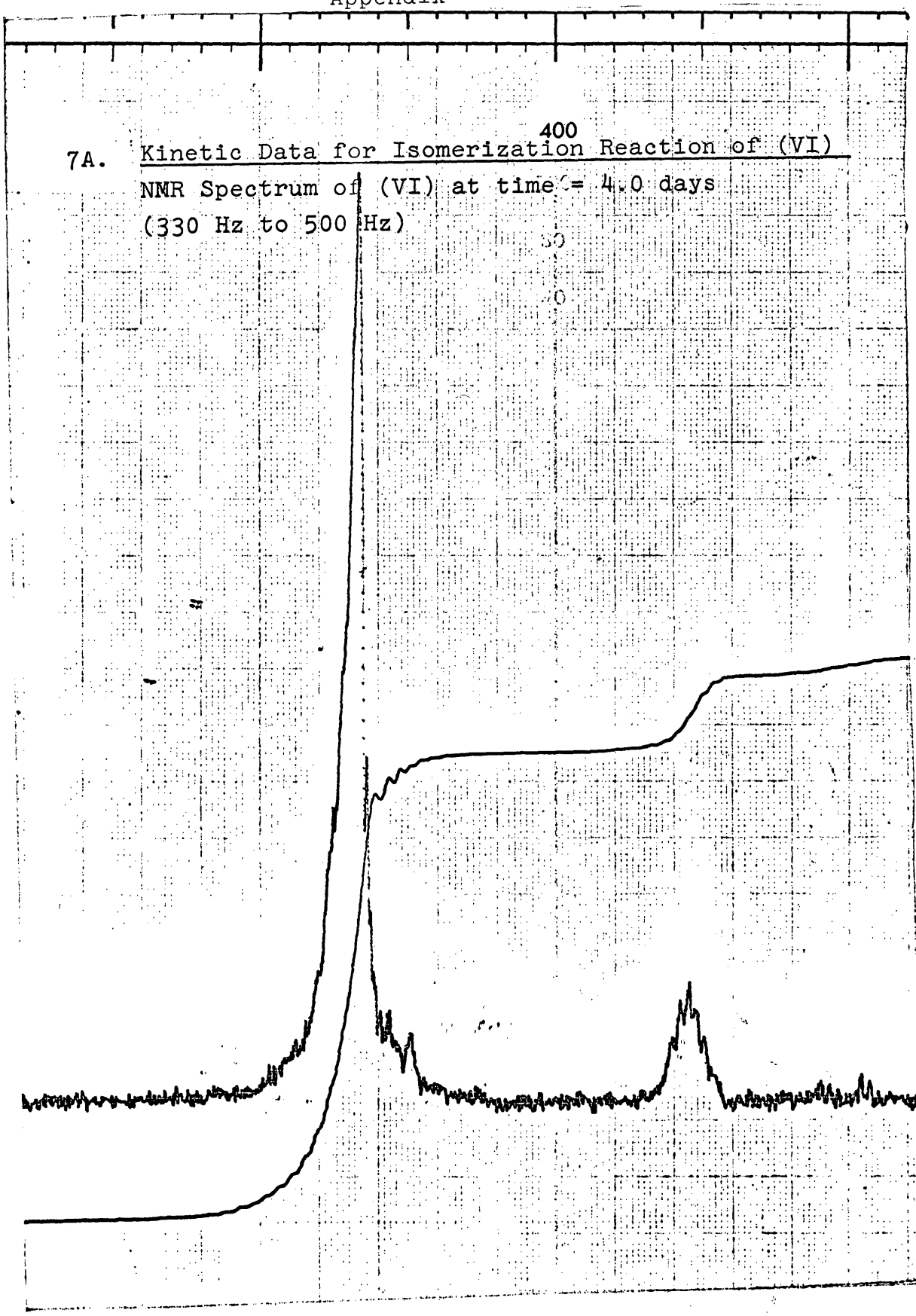
(0. Hz to 180 Hz)



7A. Kinetic Data for Isomerization Reaction of (VI)

NMR Spectrum of (VI) at time = 4.0 days

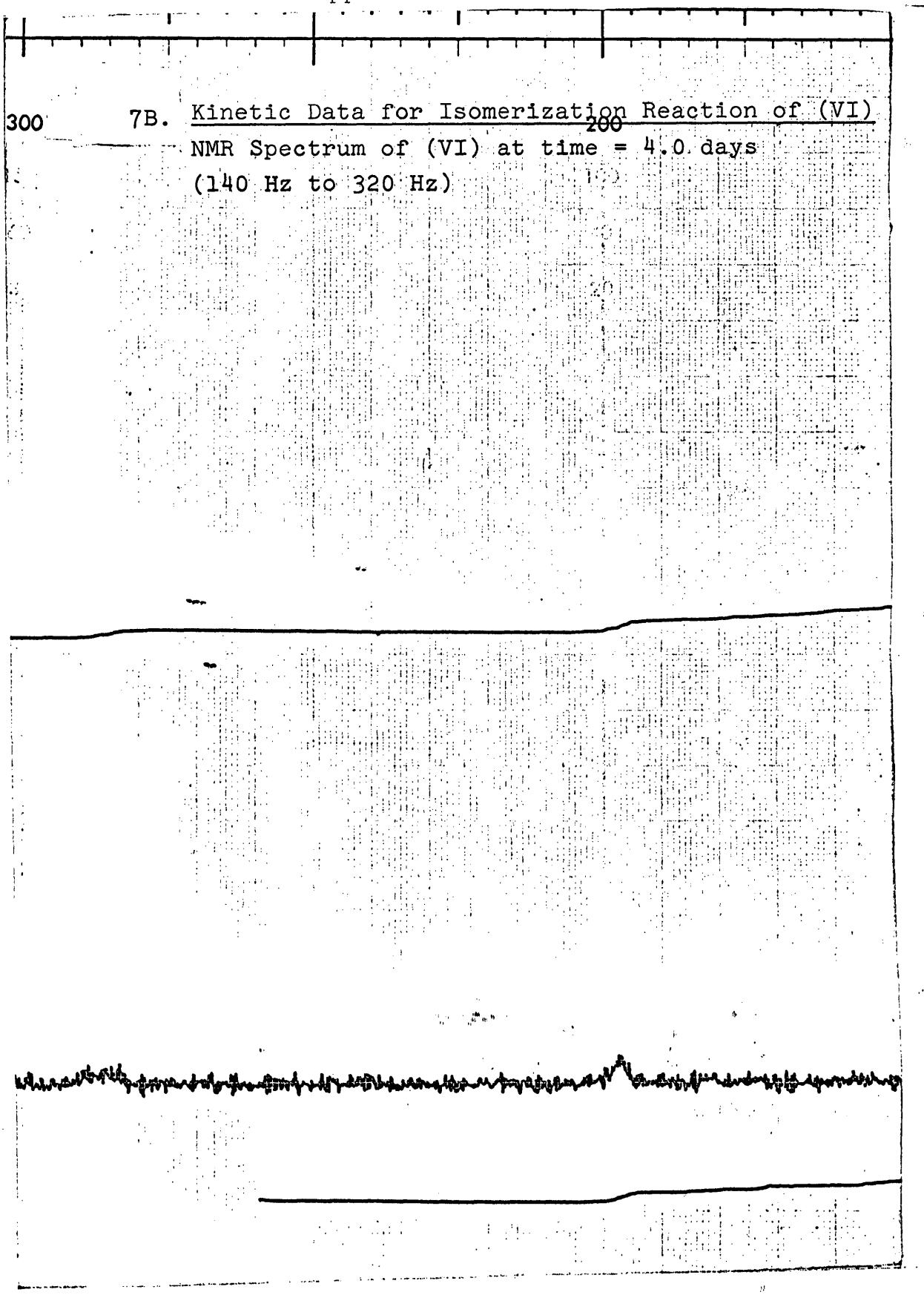
(330 Hz to 500 Hz)



7B. Kinetic Data for Isomerization Reaction of (VI)

NMR Spectrum of (VI) at time = 4.0 days

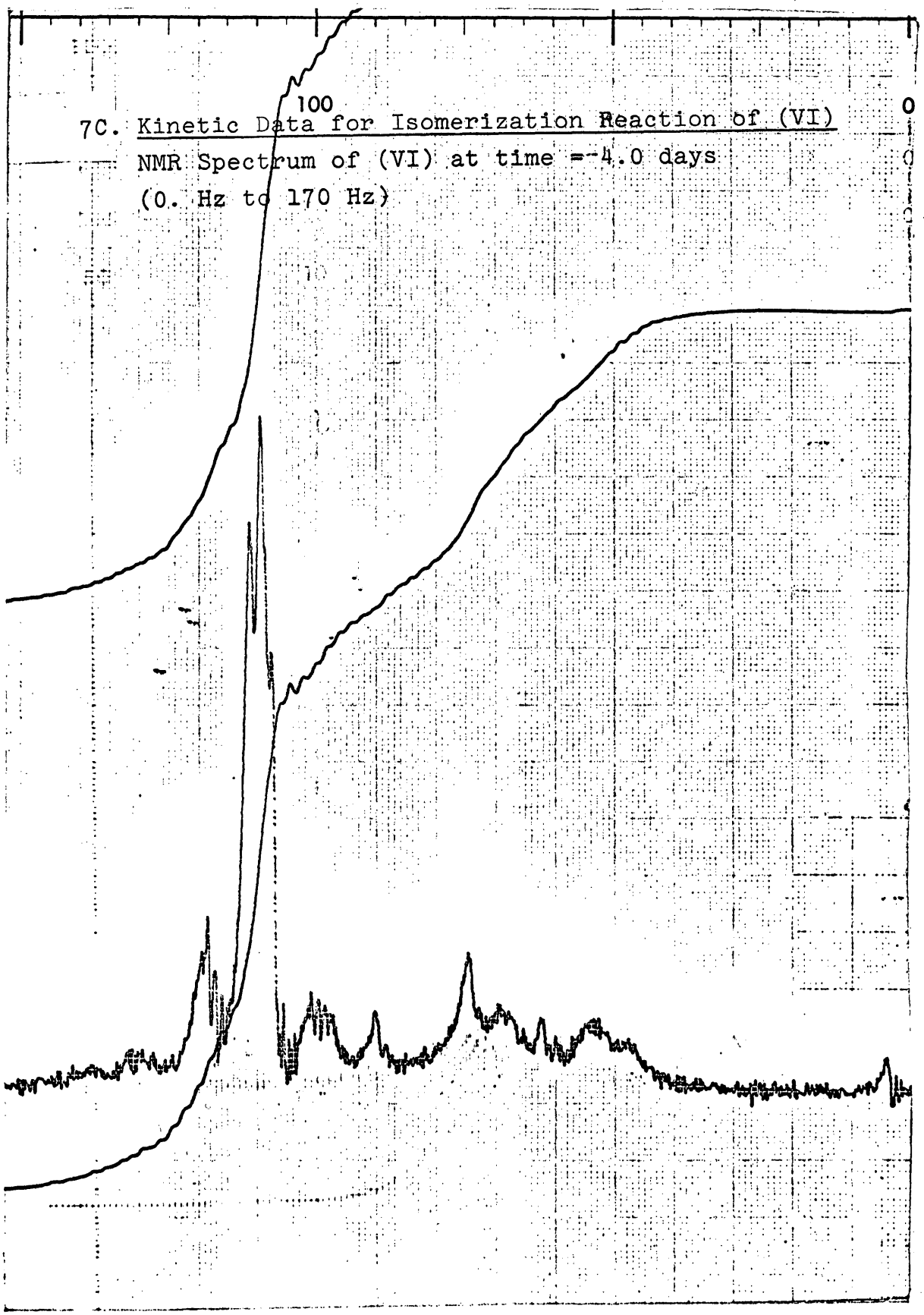
(140 Hz to 320 Hz)

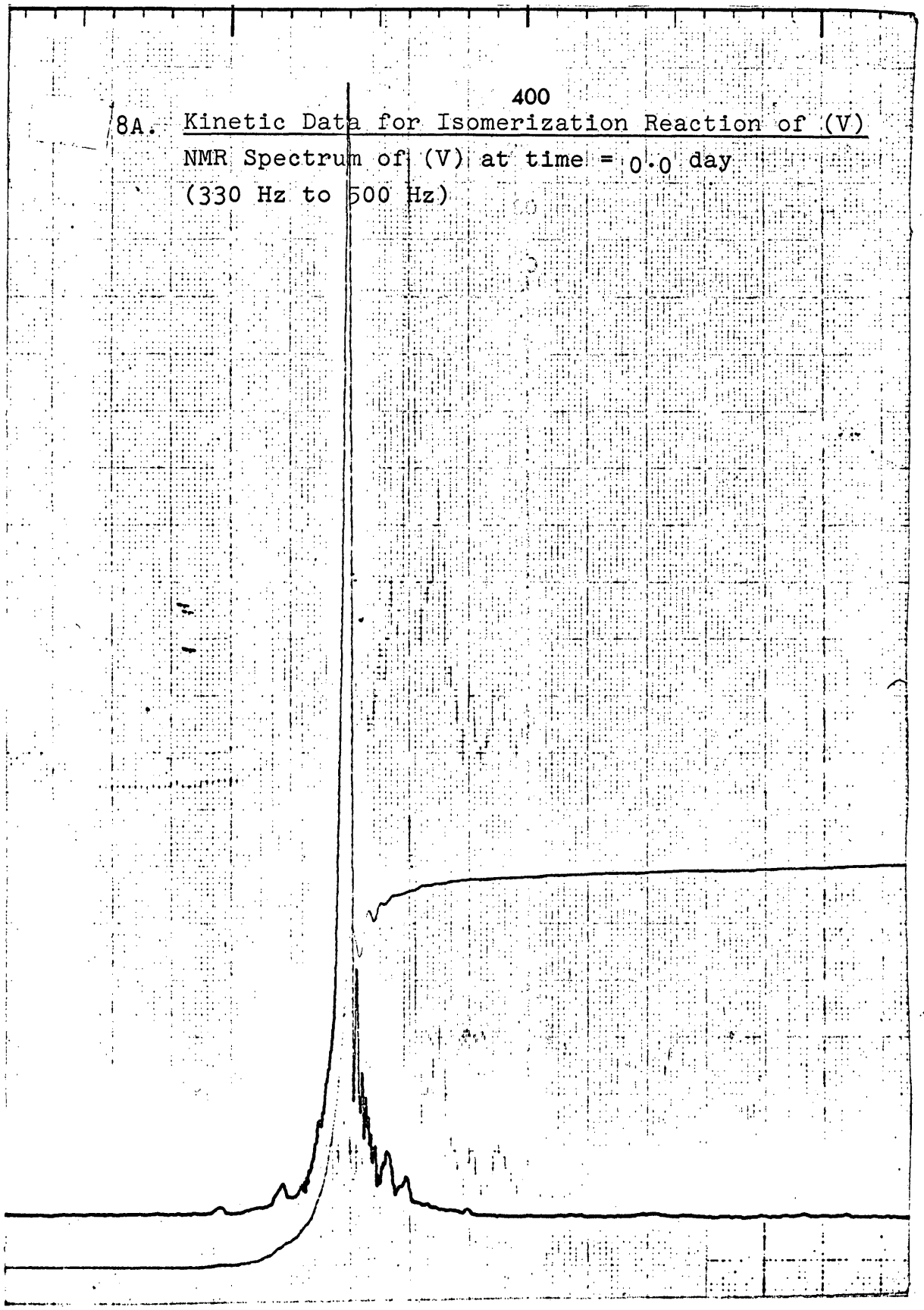


7C. Kinetic Data for Isomerization Reaction of (VI)

NMR Spectrum of (VI) at time = 4.0 days

(0. Hz to 170 Hz)





8A. Kinetic Data for Isomerization Reaction of (V)

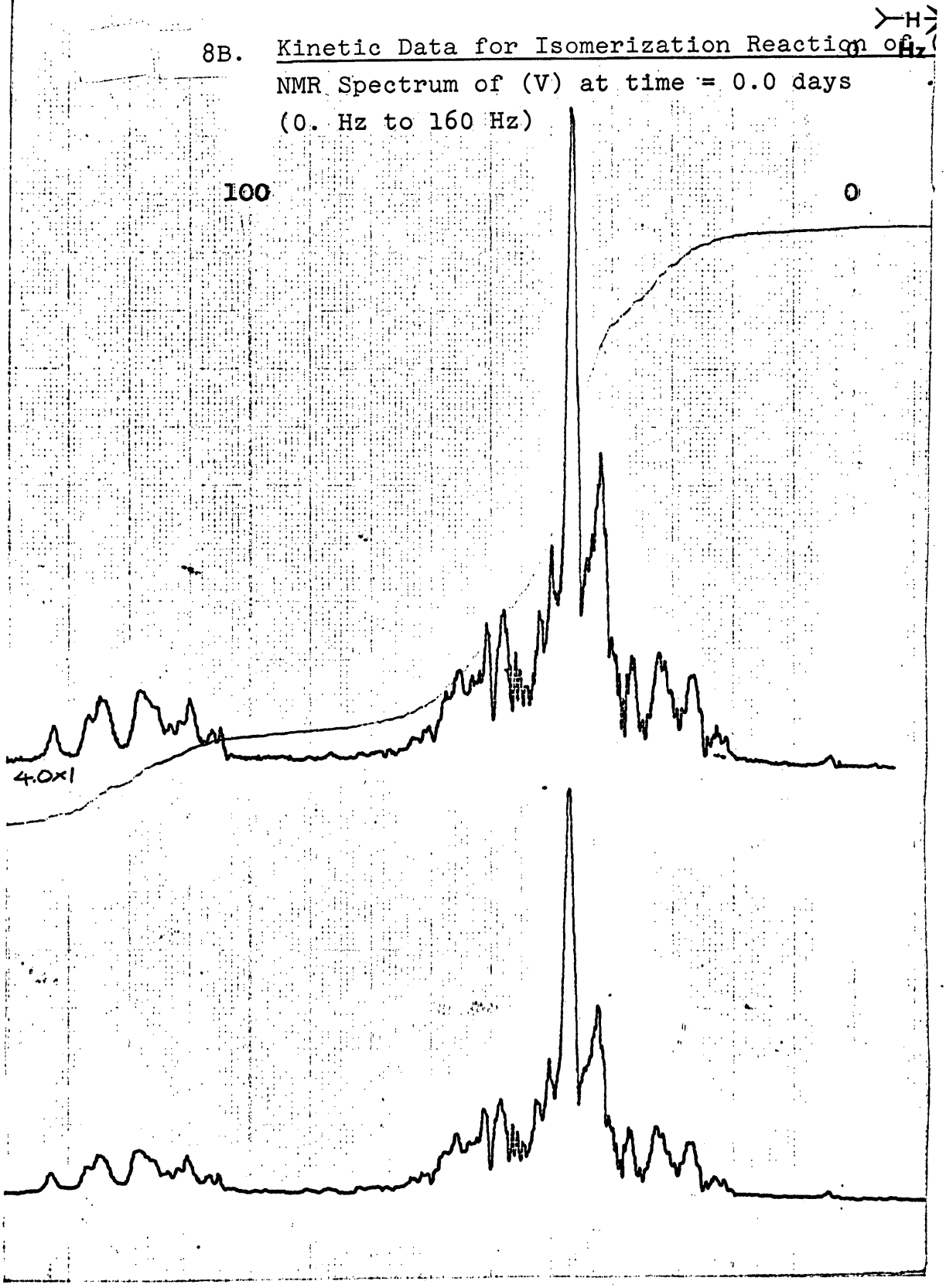
NMR Spectrum of (V) at time = 0.0 day

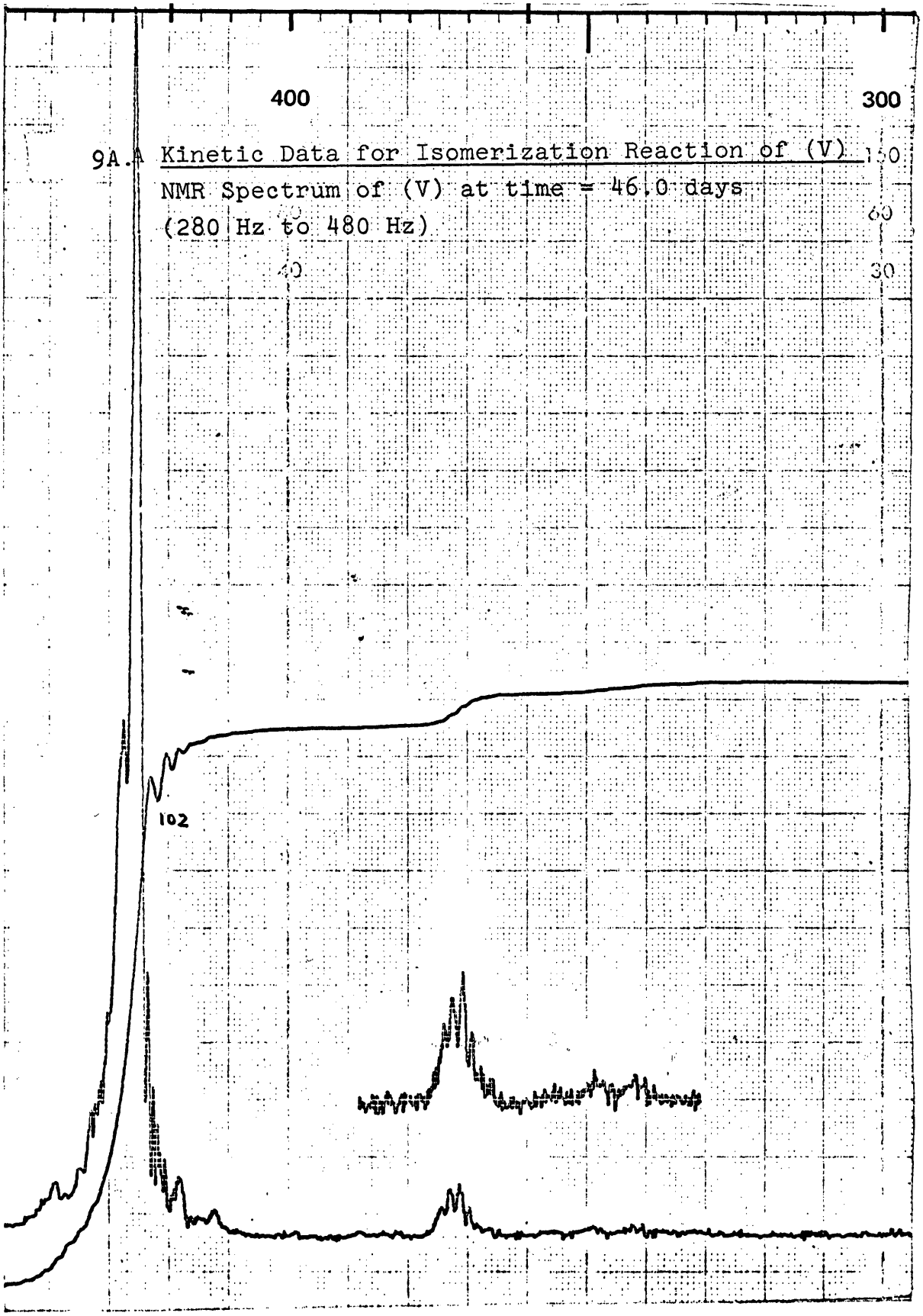
(330 Hz to 500 Hz)

8B. Kinetic Data for Isomerization Reaction of

NMR Spectrum of (V) at time = 0.0 days

(0. Hz to 160 Hz)





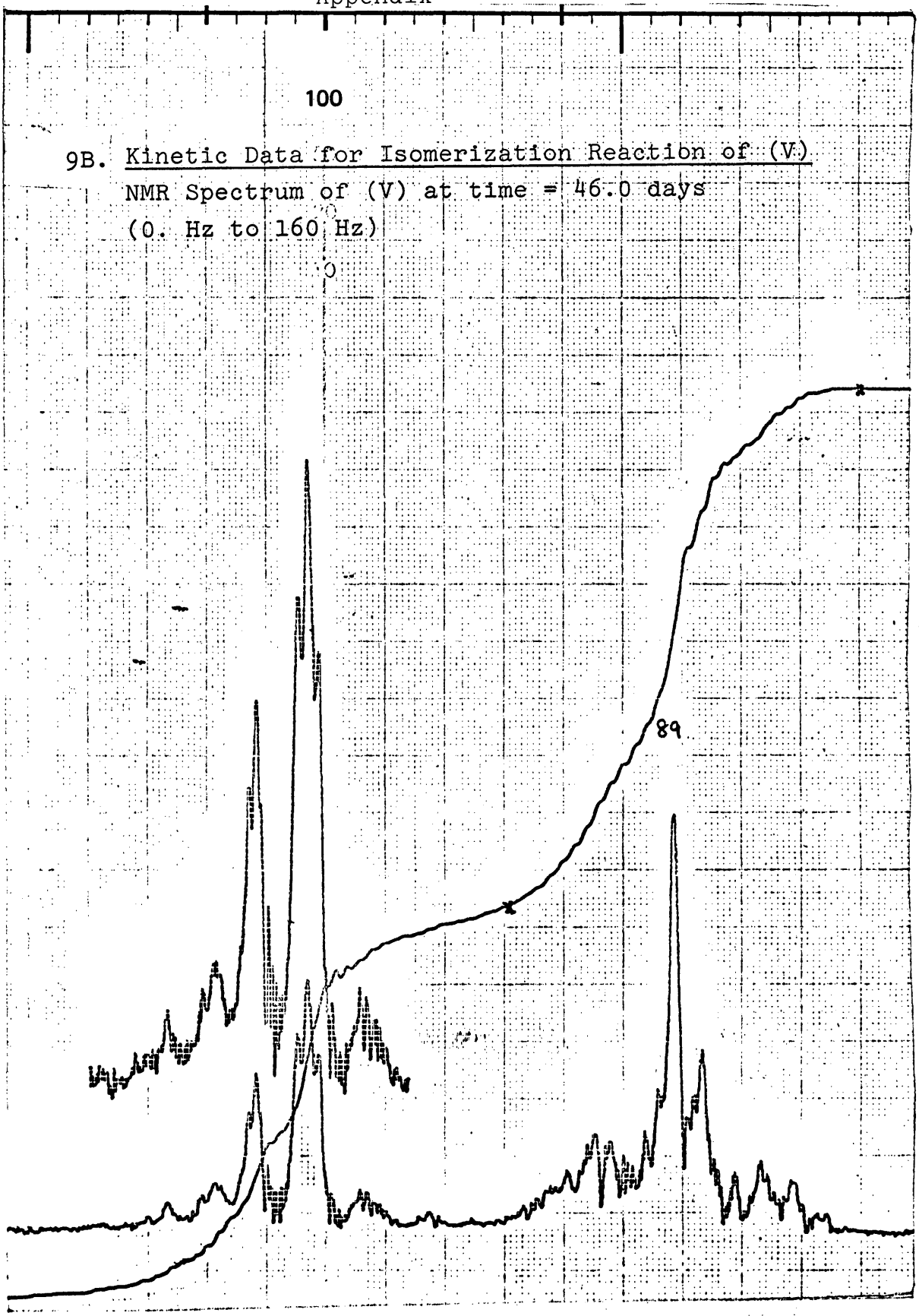
9A. Kinetic Data for Isomerization Reaction of (V)

NMR Spectrum of (V) at time = 46.0 days
(280 Hz to 480 Hz)

9B. Kinetic Data for Isomerization Reaction of (V)

NMR Spectrum of (V) at time = 46.0 days

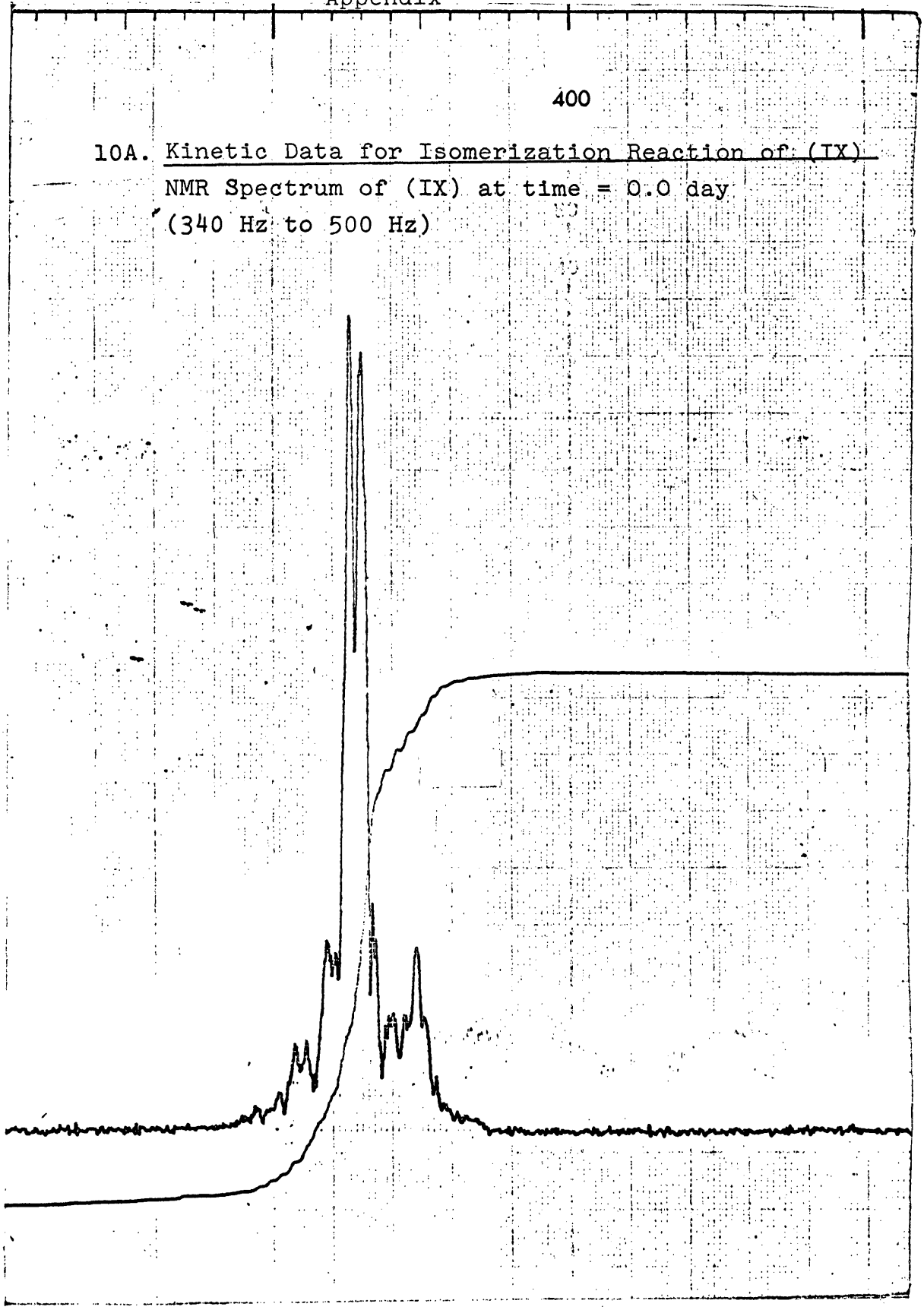
(0. Hz to 160 Hz)



10A. Kinetic Data for Isomerization Reaction of (IX)

NMR Spectrum of (IX) at time = 0.0 day

(340 Hz to 500 Hz)

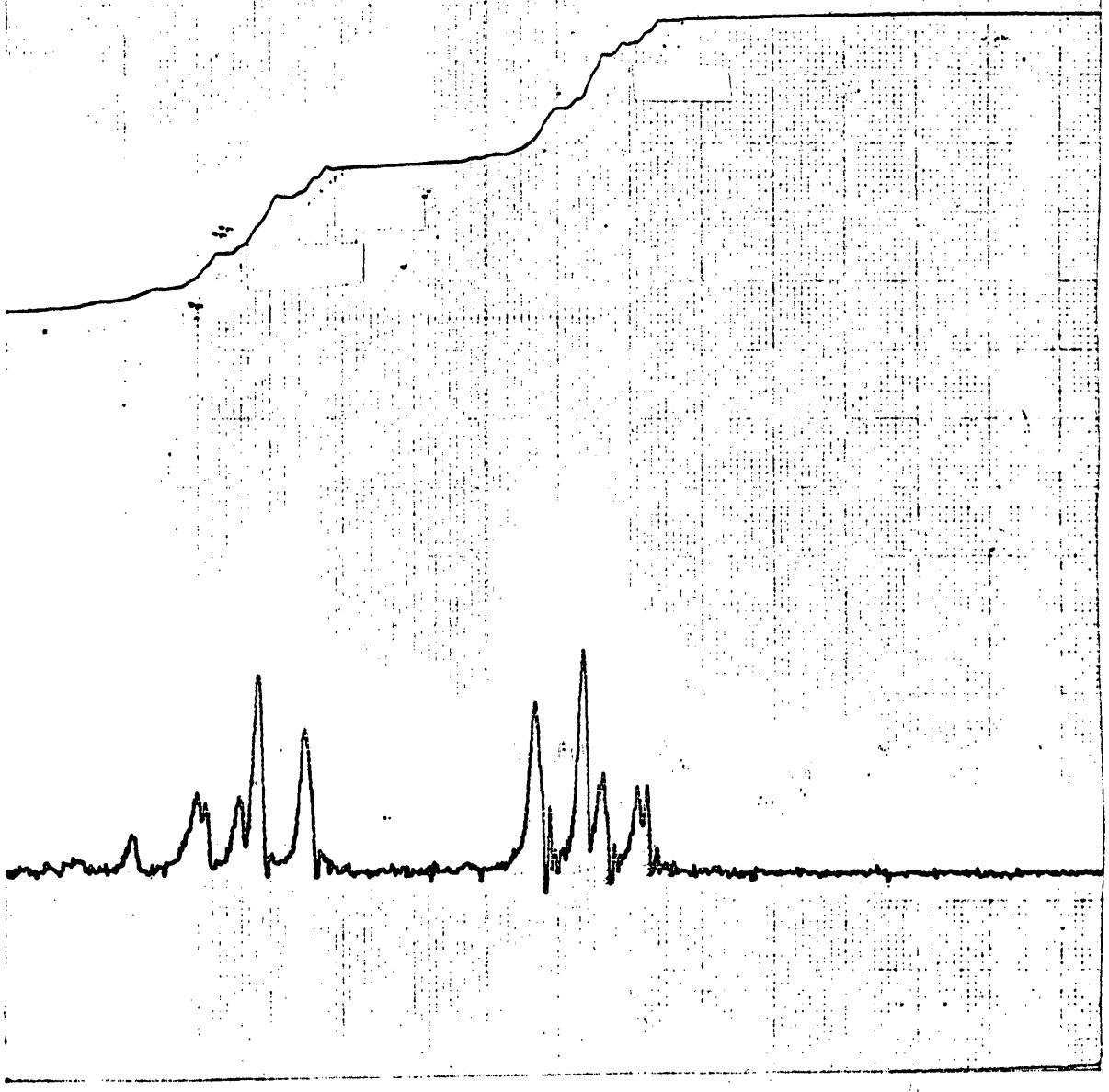


100

10B. Kinetic Data for Isomerization Reaction of (IX)

NMR Spectrum of (IX) at time = 0.0 day

(0. Hz to 200 Hz)

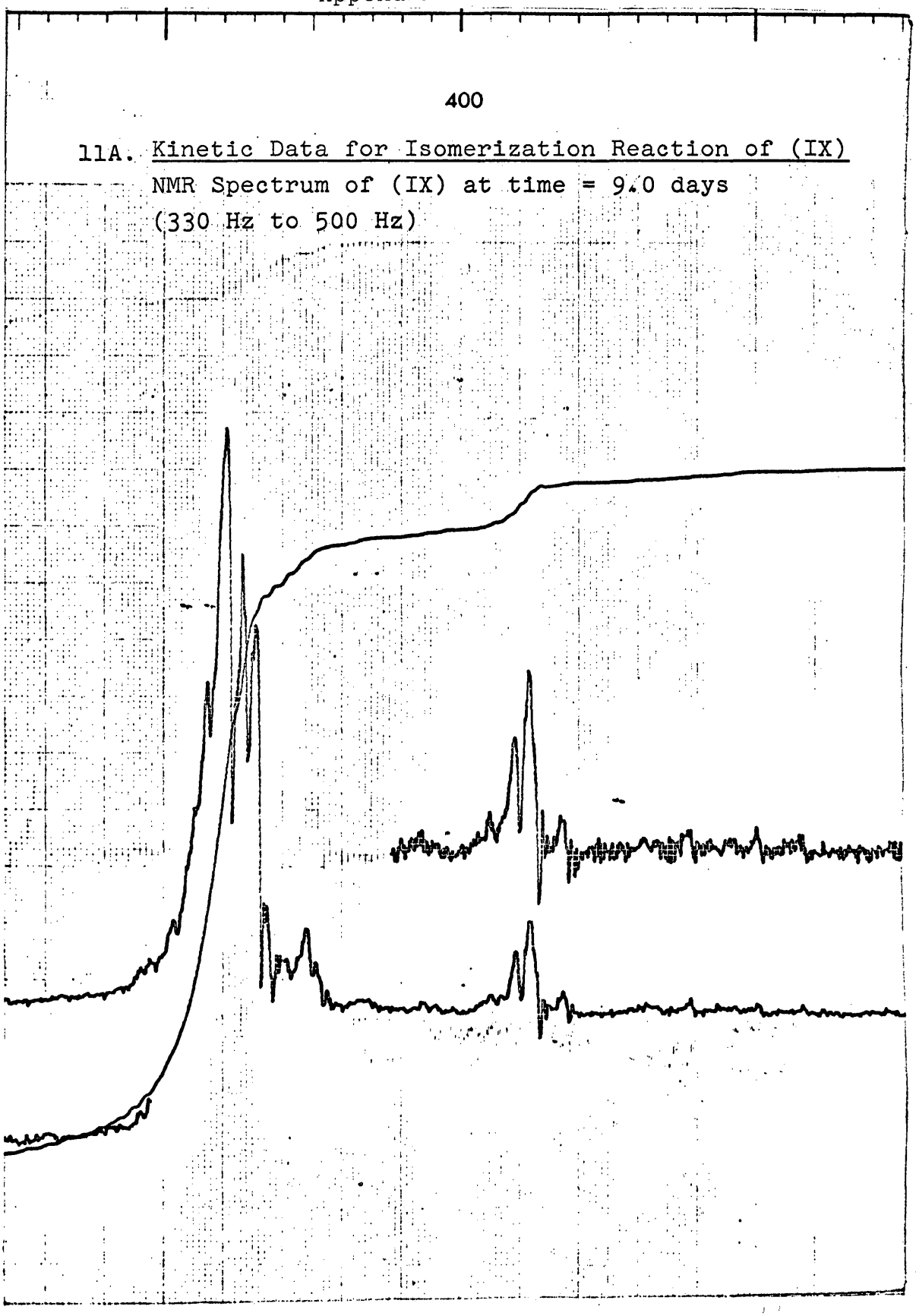


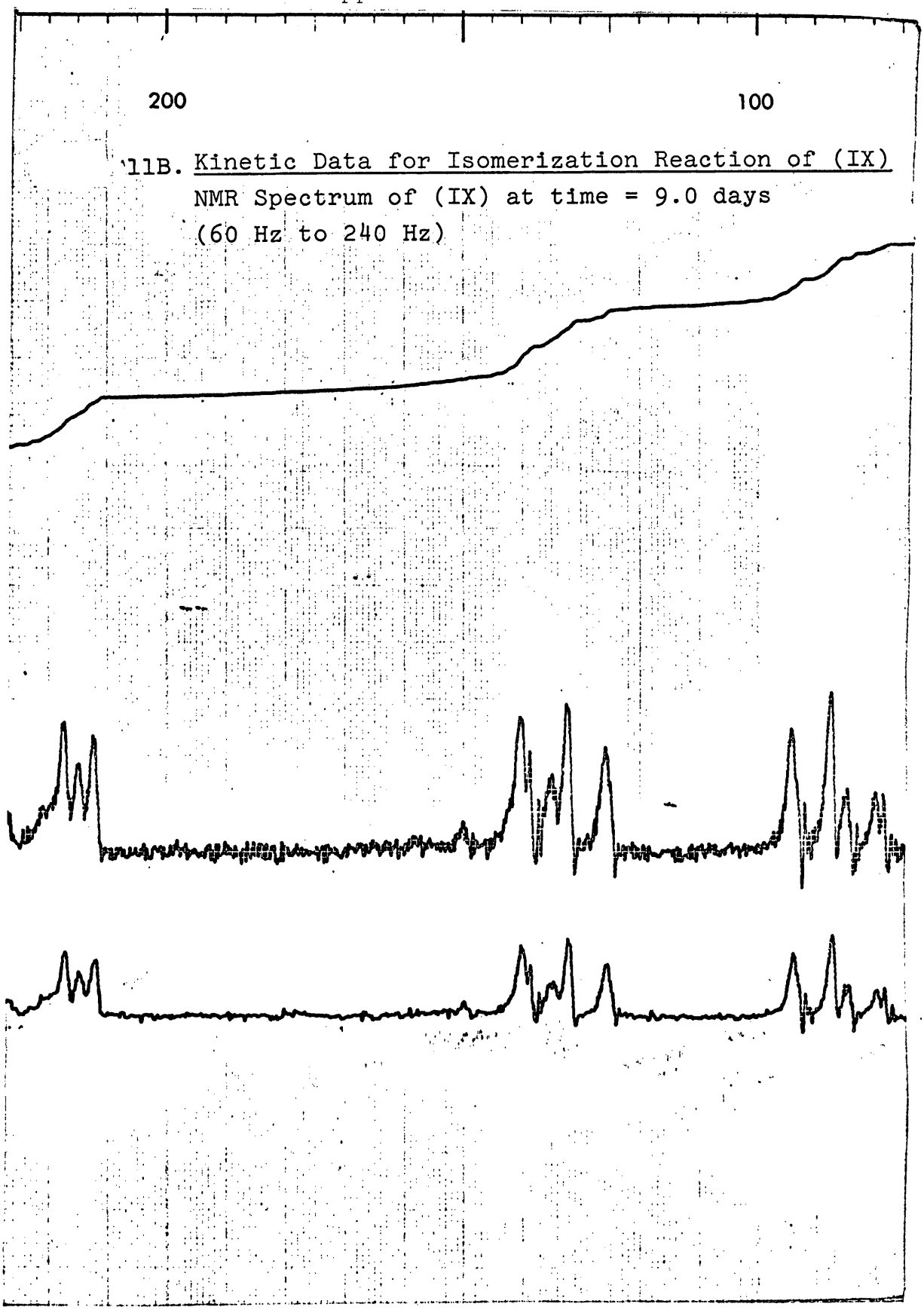
400

11A. Kinetic Data for Isomerization Reaction of (IX)

NMR Spectrum of (IX) at time = 9.0 days

(330 Hz to 500 Hz)





11B. Kinetic Data for Isomerization Reaction of (IX)
NMR Spectrum of (IX) at time = 9.0 days
(60 Hz to 240 Hz)

12A. Kinetic Data for Isomerization Reaction of (IX)

NMR Spectrum of (IX) at time = 22.0 days

(320 Hz to 500 Hz)